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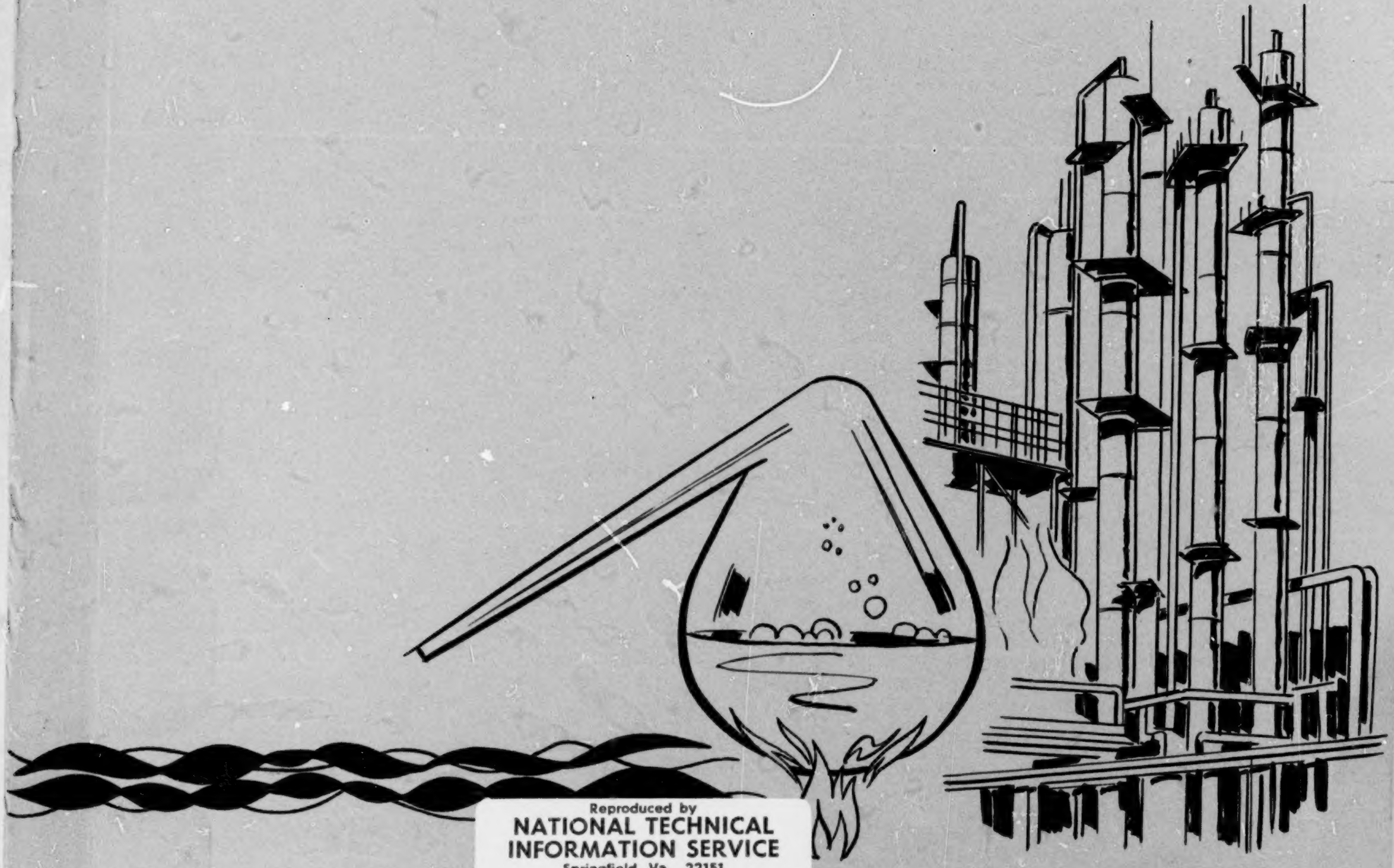

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A state-of-the-art survey was made of the water pollution problems which result from the production of inorganic fertilizers and phosphate rock. Information required to complete the study was obtained through an extensive literature search, questionnaires sent to the major fertilizer producers, and visits to selected production plants. Ninety eight plants representing thirty three different companies were surveyed. Production figures since 1940 and estimates of production through 1980 were accumulated for phosphate rock and the major fertilizer products. The specific production operations which are the principal generators of contaminated waste waters were identified, and the waste water volumes and compositions for each operation were determined wherever possible. The capability of current technology to treat and control the contaminated waste waters generated by the fertilizer industry was evaluated. Problem areas where additional research and development effort is needed to provide adequate control of waste water discharge were identified. ~~(Fullam - Battelle-Northwest)~~ (EPA abstract)

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INORGANIC FERTILIZER AND PHOSPHATE MINING INDUSTRIES - WATER POLLUTION AND CONTROL

Prepared by

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ABSTRACT

A state-of-the-art survey was made of the water pollution problems which result from the production of inorganic fertilizers and phosphate rock. Information required to complete the study was obtained through an extensive literature search, questionnaires sent to the major fertilizer producers, and visits to selected production plants. Ninety eight plants representing thirty three different companies were surveyed. Production figures since 1940 and estimates of production through 1980 were accumulated for phosphate rock and the major fertilizer products. The specific production operations which are the principal generators of contaminated waste waters were identified, and the waste water volumes and compositions for each operation were determined wherever possible. The capability of current technology to treat and control the contaminated waste waters generated by the fertilizer industry was evaluated. Problem areas where additional research and development effort is needed to provide adequate control of waste water discharge were identified.

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PART I INORGANIC FERTILIZER INDUSTRY

INTRODUCTION

This study was carried out for the Environmental Protection Agency by Battelle Memorial Institute under Grant No. 12020 FPD. The basic purpose of the study is to provide a state-of-the-art survey of water pollution resulting from inorganic fertilizer manufacturing operations and phosphate mining. It is intended that the study provide the following information relevant to the fertilizer industry.

1. Determination of the types and magnitude of water pollution which result from the production of inorganic fertilizers.
2. Identification of the specific process operations which are the principal generators of contaminated waste waters.
3. Evaluation of current technology for treating and controlling the contaminated waste waters generated by the fertilizer industry.
4. Identification of critical problem areas where additional research and development efforts are needed to provide adequate control of waste water discharge.

The survey covers all phases of the inorganic fertilizer industry including the mining of phosphate rock. The production of phosphoric acid and urea were also surveyed to provide a comprehensive study of the fertilizer industry. Part I of this report covers the production of fertilizer materials, while Part II covers the mining and beneficiation of phosphate rock.

The literature has been reviewed to obtain pertinent information. A great deal of information is available in the literature on fertilizer production, production processes, and plant operations. Unfortunately, the information available in the literature on pollution and its control in the fertilizer industry is relatively limited. To obtain the information required to complete the study, questionnaires were submitted to the principal fertilizer producers, and visits were made to a selected number of fertilizer plants to discuss water pollution and its control with plant operating personnel. Through use of the questionnaires and plant visits, data were accumulated from 41 different plants representing 33 different companies. Since most plants prepare more than one fertilizer product the total number of production processes surveyed totaled 98. The following list summarizes the number of sources surveyed for each major fertilizer product.

Product	No. of Plants Surveyed
Ammonia	16
Ammonium Nitrate	15
Ammonium Sulfate	3
Urea	14
Wet Process Phosphoric Acid	13
Furnace Phosphoric Acid	4
Normal Superphosphate	11
Triple Superphosphate	7
Ammonium Phosphates	11
Ammoniated Superphosphate	3
Potash	1

Much of the information on water pollution and its control in the fertilizer industry which is discussed in subsequent sections of this report was obtained from the plant survey. Information obtained from the literature is referenced. Data obtained through the plant survey are not identified as to source.

SUMMARY

The purpose of the study covered in this report was to provide a state-of-the-art survey of water pollution resulting from inorganic fertilizer manufacturing operations. The survey covered all phases of the inorganic fertilizer industry including phosphoric acid production and phosphate rock mining and beneficiation. Information needed to complete the study was obtained through a literature review, questionnaires sent to major fertilizer producers, and visits to selected fertilizer production operations for discussions with operating personnel.

The fertilizer industry is undergoing continual change and water quality standards are also changing. Therefore, it is recommended that this survey be updated at regular intervals to provide an accurate profile of water pollution control in the fertilizer industry.

Fertilizer consumption in the United States is increasing rapidly. In 1970 U.S. consumption of fertilizers was approximately 36,000,000 short tons. It is estimated that by 1980 fertilizer consumption will increase to about 70,000,000 short tons annually. Nitrogen fertilizers constitute the largest share of the fertilizer market, and phosphate and potash fertilizers the bulk of the remaining market. The importance of nitrogen fertilizers is expected to increase in the future. The types and grades of fertilizers used are continually changing, and the emphasis is on the production of higher nutrient content materials. Production processes are undergoing continual change to accommodate the changing market requirements.

The fertilizer industry consumes large volumes of water. It is estimated that the gross water requirements of the industry exceeded one trillion gallons in 1970. Water recycle is widely practiced by the fertilizer industry industry, and 75-80% of the gross water requirements were supplied by recycled water. Recycling of water should increase in the future, and the ultimate objectives of many fertilizer producers is to achieve complete closed loop water reuse. Of all the water used by the industry, 70-80% is for cooling purposes.

A great many different types and grades of fertilizers are produced in the United States. Many of these products are prepared by the blending of the principal fertilizer materials to give the desired compositions. The number of different straight and mixed (nonblended) fertilizers produced on a large scale are relatively few. They are:

Ammonia
Ammonium Nitrate
Ammonium Sulfate
Urea
Nitrogen Solutions

Potassium Chloride

Phosphate Rock
Normal Superphosphate
Triple Superphosphate
Ammonium Phosphates
Ammoniated Superphosphate

Phosphoric acid, while not used directly as a fertilizer to any extent, is an indispensable intermediate in phosphate fertilizer production.

Each of the major fertilizer materials can be produced by two or more processes or process variations. It was impossible within the limits of this study to evaluate each process, and the possible variations, for its effect on the environment. Instead, a typical or standard process was defined for each major fertilizer product. A typical flowsheet was prepared for each product and the specific operations in the flowsheet which generate contaminated waste waters were identified. Using the typical flowsheets and literature and plant survey data, typical waste stream volumes and compositions were determined for each of the major fertilizer products.

Waste water discharges from a fertilizer plant can be broken down into four general types:

Cooling water
Steam condensate
Process Effluents
Sanitary wastes

The process effluents can be further subdivided into five general classes:

By-product streams
Scrubber solutions
Process spills
Equipment cleaning (wash) solutions
Barometric condenser water

One or more of these waste streams will usually be generated in any fertilizer production operation.

A review of the fertilizer industry reveals that inorganic materials are the major pollutional problems encountered in fertilizer plant waste water. Conventional pollutional parameters such as BOD, COD, and coliform are relatively unimportant because of the low organic content of most fertilizer plant waste waters. The principal contaminants found in most fertilizer plant waste waters are plant nutrients such as nitrogen (as ammonia and nitrate) and phosphates, and toxic materials such as fluoride, chromate, and elemental phosphorus. Thermal pollution is also a problem which must be considered. The only organic materials which present a major disposal problem are lubricating oils. Urea, monoethanolamine, and organic biocides are present in certain waste waters but do not present a major disposal problem at the present time. On an overall basis nitrogen in nitrogen fertilizer plant waste waters and phosphate and fluoride in phosphate fertilizer plant waste waters present the major contaminants which must be controlled by the fertilizer industry. Nonfertilizer additives such as pesticides and herbicides, which may be added to certain fertilizer formulations, were not considered in this study.

In the production of nitrogen fertilizers most plants currently rely on disposal by dilution for control of plant effluents. Treatment of these process wastes is usually restricted to the use of separators for oil removal and settling ponds for solids removal and cooling. Chemical treatment, using sulfur dioxide and lime, is usually provided for chromate removal from cooling water blowdown. While disposal by dilution is currently acceptable in many areas for disposing of nitrogen fertilizer plant waste waters, it is not acceptable in some locations (and will become less acceptable in other areas in the future). Methods for nitrogen removal (principally ammonia and nitrate) are needed by the industry to treat the waste waters when disposal by dilution is inadequate or unacceptable. Gas stripping is used for ammonia removal in some plants, but does not provide the degree of ammonia removal which may be required. A study supported by the EPA (Grant No. 12020EGM) is currently underway at the Tyner, Tennessee plant of Farmers Chemical Association, Inc., to evaluate the use of ion exchange to remove ammonia and nitrate from fertilizer plant waste waters.

Phosphoric acid and phosphate fertilizer plant waste waters normally require treatment for fluoride and phosphate removal. When a gypsum pond is available, all contaminated waste waters normally discharge to the gypsum pond. Treatment of the pond water discharge by lime neutralization reduces the fluoride and phosphate concentrations to acceptable levels under current water quality standards.

When a gypsum pond is not available, other methods for treating phosphate fertilizer plant waste water are needed. Fluoride is the principal problem, and is usually handled by recovering the fluoride as a salable by-product.

Data on the cost of providing adequate control and treatment of fertilizer plant waste waters is relatively scarce. Information obtained from the plant survey shows that expenditures for treating nitrogen fertilizer plant waste waters ranges from 0 to $0.78 per ton of product. These costs reflect the comparatively low level or lack of treatment provided these waste streams. The cost of treating the waste waters from phosphoric acid and phosphate fertilizer plants ranges from $0.90-$3.00 per ton of P_2O_5 product and averages about $1.90 per ton of P_2O_5.

Several problem areas have been identified where additional research and development effort is required to help the fertilizer industry meet current and future water quality standards. The critical areas include:

1. The definition of realistic water quality standards.

2. The development and application of suitable processes for ammonia removal from waste waters.

3. The development and application of processes for removing other nitrogen compounds from waste waters.

4. Development of methods for utilizing by-product gypsum from wet-process phosphoric acid production.

5. Development of an improved process for removal and possible recovery of fluoride from waste waters.

6. Development of an improved process for removal and possible recovery of phosphate from waste waters.

7. Determination of the mechanisms involved in phosphate removal by lime neutralization.

8. Development of reliable, continuous, monitoring methods for principal contaminants found in fertilizer plant waste waters.

Study in these critical areas will help provide the fertilizer industry with the technology needed to maintain adequate control over waste waters generated by the industry.

DESCRIPTION OF THE INORGANIC FERTILIZER INDUSTRY

The fertilizer industry in the United States is an industry undergoing continuing change and expansion. Production and use of fertilizers have experienced tremendous growth especially over the past thirty years. The types and grades of fertilizers produced are continually changing. Natural fertilizer materials have been almost completely supplanted by manufactured products. New mixed fertilizers are continually being introduced. New processes are being developed to meet changing product requirements, and the entire fertilizer industry is becoming much more complex.

At least 13 elements, in addition to carbon, hydrogen, and oxygen, have been definitely identified as essential to plant growth. Most of these elements are required in relatively small amounts. Three elements, however, (nitrogen, phosphorus, and potassium) are required in large quantities to sustain good plant growth. Supplying adequate quantities of these three primary nutrients is the basic purpose of the fertilizer industry. Of the three elements, nitrogen is required in the greatest quantity and phosphorus in the smallest quantities. Some authorities predict that, regardless of plant needs, the three nutrients will eventually be used on a 1:1:1 basis.

Production and consumption of fertilizers to supply the three primary nutrients has grown very rapidly. Figure 1 shows the consumption of fertilizer materials in the United States since 1940.(1,2,3,4,5) Between 1940 and 1970 fertilizer consumption increased by over 400%. Based on a number of estimates, it appears that fertilizer consumption in the United States should increase by about 100% between 1970 and 1980.(1,2,6,7,8) Nitrogen consumption is expected to grow at the fastest rate and phosphate consumption at the slowest rate. United States production of fertilizer materials (except potash) normally exceeds consumption since exports usually exceed imports. This trend is expected to continue in the future. In the case of potash it is likely that consumption will exceed domestic production for a number of years because of the large-scale importation of Canadian potash.

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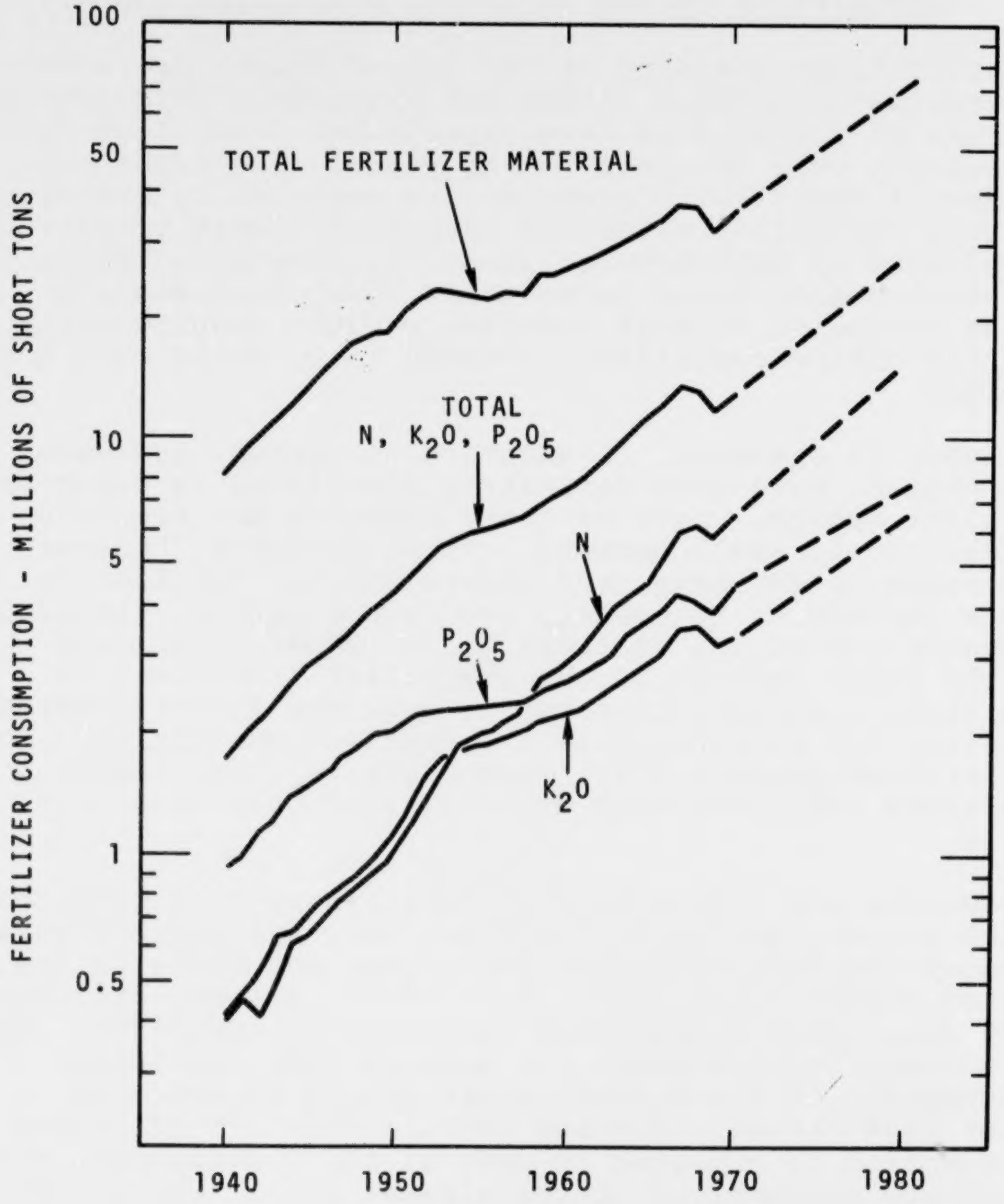


FIGURE 1 FERTILIZER CONSUMPTION IN THE UNITED STATES (1,2,3,4,5,6,7,8)

Fertilizers are generally divided into two major types: straight fertilizers and mixed fertilizers. Straight fertilizers are those fertilizer materials which contain only one major plant nutrient. The principal straight fertilizers produced in the United States are listed in Table 1.

Mixed fertilizers are those materials which contain two or more primary nutrients. Mixed fertilizers can be prepared by the simple mechanical blending of straight fertilizers or by reacting the fertilizer materials chemically to produce the desired fertilizer products. Typical of the mixed fertilizers produced by chemical reactions are the ammonium phosphates and ammoniated superphosphate. The two methods can be combined to produce a three-nutrient fertilizer. For example, in the production of ammoniated superphosphate potassium chloride can be added to the reaction process to give an N-P-K fertilizer. The potassium chloride does not enter into chemical reactions but simply blends into the reaction product.

In the case of straight nitrogen fertilizers, most of the materials are consumed in direct application and only about 32% are consumed in mixed fertilizers.(2,9) This is due primarily to the widespread use of anhydrous ammonia, aqua ammonia and nitrogen solutions in direct applications. The percentage of nitrogen consumed in mixed fertilizers is not expected to change significantly in the future.

The situation is reversed in the case of phosphorus and potassium. At present about 86% of the phosphorus used in fertilizer applications is in the form of mixed fertilizers, and the percentage is expected to increase in the future.(2,9) In the case of potassium, the percentage consumed in mixed fertilizers is about 78%, but is expected to decrease somewhat in the future.(2,9)

The process of mechanically blending straight fertilizers to produce mixed fertilizers has undergone a significant change in recent years. Originally, the blending was carried out by dry mixing of nongranular straight fertilizers. The products obtained were unsatisfactory for a number of reasons, and this type of blending operation has been almost completely replaced by other processes.

TABLE 1

PRINCIPAL STRAIGHT AND MIXED FERTILIZERS PRODUCED IN THE UNITED STATES

Nitrogen Fertilizers

- Ammonia
- Ammonium Nitrate
- Ammonium Sulfate
- Urea
- Nitrogen Solutions

Phosphate Fertilizers

- Phosphate Rock
- Phosphoric Acid
- Normal Superphosphate
- Triple Superphosphate

Potash Fertilizers

- Potassium Chloride

Mixed Fertilizers*

- Ammonium Phosphates
- Ammoniated Superphosphate

*Does not include blended fertilizers and liquid mixes.

With the advent of granular fertilizer products, the so called "bulk blending" process has become extremely important. This process involves simply the mechanical mixing of granular fertilizer materials to give the desired fertilizer composition. The materials normally used in the bulk-blending operation are potassium chloride, ammonium phosphates, triple superphosphate, ammonium sulfate, ammonium nitrate, and urea. The use of granular materials eliminates many of the disadvantages of the original dry mix process, and as a result the production of bulk-blended fertilizers has increased very rapidly. This can be seen by considering the rate at which bulk-blend plants have increased in the United States.(9)

Year	Estimated Number of Bulk-Blend Plants in U.S.
1960	466
1964	1536
1966	3152

The bulk-blend plants are usually small and serve only a limited area. They are concentrated principally in the major consumption areas of the midwest.

Another recent development is the increased use of liquid-mixed fertilizers. They are prepared primarily by blending aqueous solutions of various fertilizers to obtain the desired composition. Some liquid mix plants dissolve combinations of solid fertilizers to obtain the required compositions. Like bulk-blend plants, liquid mix plants are quite small and designed to serve limited areas. The number of liquid mix plants in the United States is significantly smaller than bulk-blend plants, but still represents a sizable fertilizer output.(9)

Year	Estimated Number of Liquid Mix Plants in U.S.
1960	380
1964	720
1966	1231

In the past the production of nitrogen fertilizers, phosphate fertilizers and potash were relatively separate operations. The limited amounts of mixed fertilizers produced were made primarily by shipping potash and nitrogen fertilizers to mixed-fertilizer plants for blending with phosphate. Production of mixed fertilizers such as ammoniated superphosphate and the ammonium phosphates was almost always carried out at phosphoric acid-phosphate fertilizer plants. Potash production is still completely separate from other fertilizer production. However, the recent trend is to combine nitrogen and mixed fertilizer production at large nitrogen fertilizer complexes.

In certain instances nonfertilizer materials, such as herbicides or pesticides, may be added to fertilizer formulations. Additions of these materials to the fertilizers and their possible entry into fertilizer plant waste waters was not covered in this study.

NITROGEN FERTILIZER INDUSTRY

Nitrogen is required in larger quantities for good plant growth than any other nutrient. Since 1957 fertilizer nitrogen consumption in the United States has exceeded both phosphate and potash on a tonnage basis. The principal sources of fertilizer nitrogen have changed drastically during this century. Prior to 1900 almost all fertilizer nitrogen used in the United States came from natural organic materials. Between 1900 and 1920 natural nitrate deposits were an important source of fertilizer nitrogen, and for many years by-product ammonia from coke-oven gas was an important factor in the fertilizer industry. With the development of the Haber-Bosch process for ammonia production, atmospheric nitrogen became the principal source of fertilizer nitrogen. Slack(9) ranks the various sources of fertilizer nitrogen in the United States at the current time as follows:

Source	Percent of Fertilizer Nitrogen Supplied
Natural Organics	1
Sodium Nitrate	2
Coal	3
Atmospheric Nitrogen	94

The economic development of the Haber-Bosch process for production of ammonia from nitrogen and hydrogen has resulted in ammonia becoming the most important fertilizer material in the United States. Not only is ammonia used on a very large scale as a fertilizer, but it also serves as a raw material for the preparation of almost all other nitrogen containing fertilizers produced in the United States. The tremendous growth in synthetic ammonia production since 1940 is shown in Figure 2.

Estimates of future production indicate that ammonia should continue to experience the same rapid growth.(2,10) The importance of ammonia to the fertilizer industry can be seen by referring to Table 2 which lists the quantities of ammonia used in various fertilizer processes in the United States.

Total ammonia consumption in the United States in 1968 was estimated to be 12,032,000 short tons.(10) Of this amount, 80.6% was used in fertilizer applications. The rest was used principally in urea, nitric acid, and ammonium nitrate production for nonfertilizer applications.

Location of ammonia plants is dependent on two factors, availability of raw materials and accessibility to the market. Of the two, a raw material supply is the most important. Since atmospheric nitrogen is readily available anywhere, a source of hydrogen is of prime importance in ammonia production. In the United States natural gas and petroleum fractions serve as the principal sources of hydrogen. As a result ammonia plants are located most heavily in those areas where natural gas and petroleum fractions are readily available. Louisiana, Texas, California, Iowa, Mississippi, and Arkansas are currently the major ammonia producing states.(2) The state of Iowa is also the largest consumer of fertilizer nitrogen. In total, there are approximately 70 companies producing ammonia in plants located in 30 different states. The location of the major ammonia plants are shown in Figure 3. It is estimated that the total ammonia production capacity of the United States as of January 1971, was 18,700,000 short tons per year.(10)

An interesting facet of ammonia production has been the trend to very large capacity plants. In 1955, 300 tons per day was considered to be a large plant. Today 1000 tons-per-day plants are not uncommon and plants as large as 1500 tons-per-day have been built. The economic advantage of very large plants is slowly forcing the shut-down of

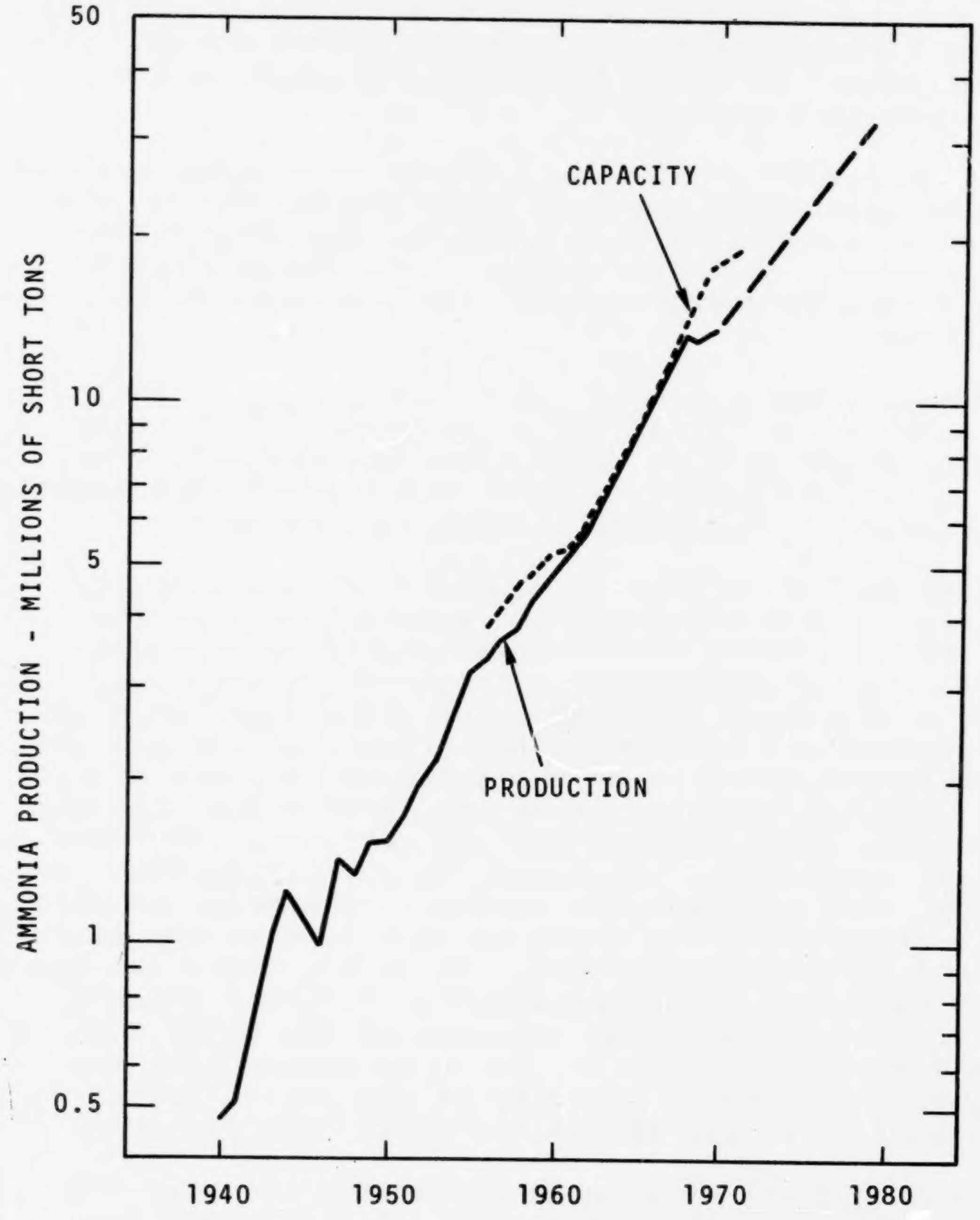


FIGURE 2 SYNTHETIC AMMONIA PRODUCTION IN THE UNITED STATES (1,2,3,4,5,10)

TABLE 2

AMMONIA CONSUMED IN UNITED STATES IN FERTILIZER APPLICATIONS

	NH_3 Used (thousands of Short Tons)		
Fertilizer Product	1960	1965	1968
Direct Application NH_3	837	1877	3375
Ammonium Nitrate	1252	1838	2164
Ammonium Sulfate	388	707	751
Ammonium Phosphates	228	705	1425
Nitrogen Solutions and Mixed Fertilizers	432	428	560
Urea	309	581	1285
Other Fertilizers	31	99	136
TOTAL	3477	6235	9696

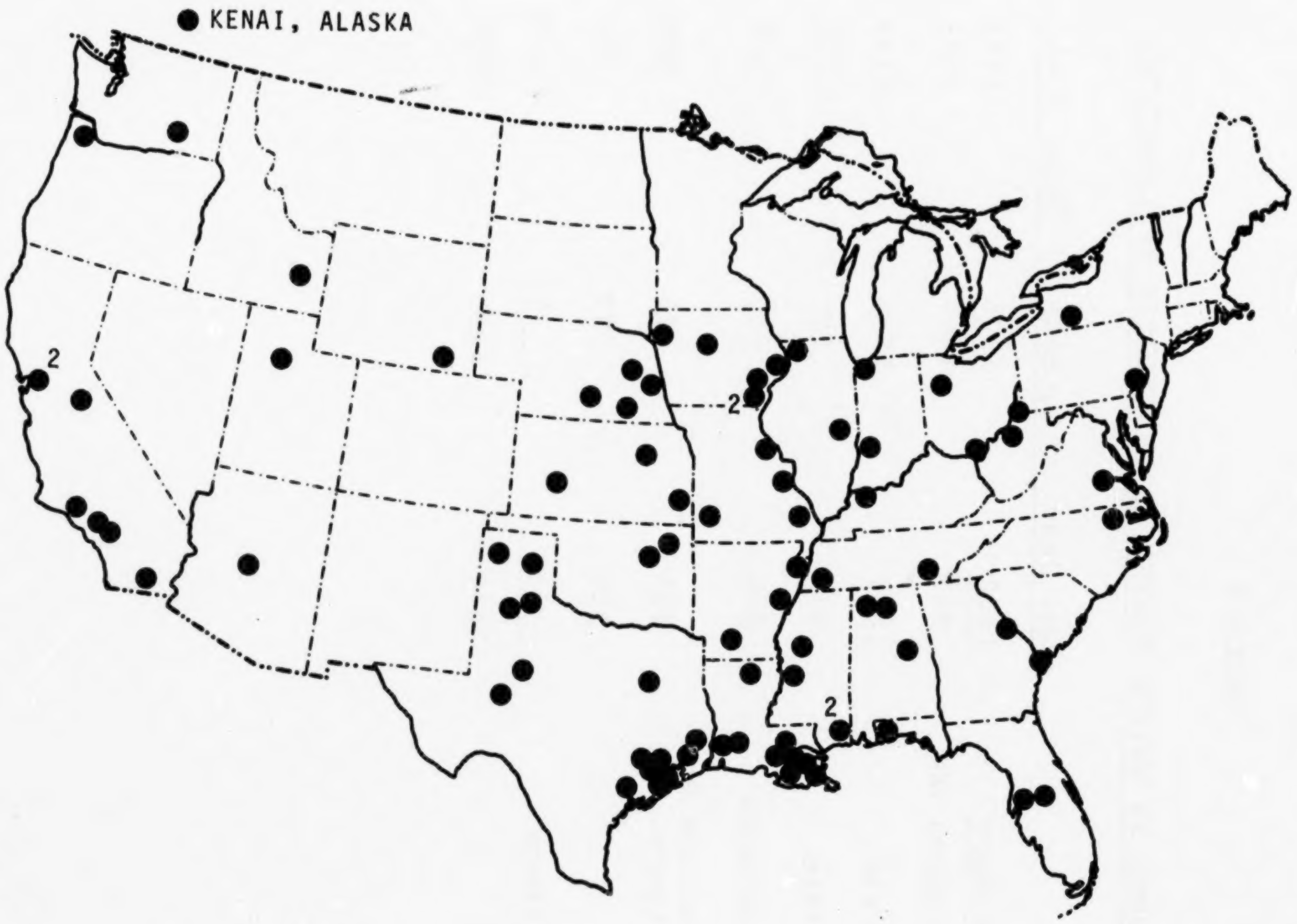

KENAI, ALASKA
2
2
2

FIGURE 3 LOCATION OF MAJOR AMMONIA PLANTS IN THE UNITED STATES

many older, smaller plants. The high nitrogen content of ammonia and improved shipping procedures makes it economical to produce ammonia in large plants and ship for substantial distances to the markets.

As stated previously, ammonia serves as a raw material in the production of almost all nitrogen fertilizers. On a tonnage basis the most important nitrogen fertilizers, in addition to ammonia, are ammonium nitrate, ammonium sulfate, and urea. United States consumption of these materials in fertilizer applications is shown in Figure 4. The data presented are for total consumption of each material and include the tonnages used in direct application and in the preparation of mixed fertilizers.

Ammonium nitrate ranks second only to ammonia as a source of fertilizer nitrogen. During the 1950's ammonium nitrate was the principal source of fertilizer nitrogen but has now been displaced by ammonia. Long range predictions show that ammonium nitrate should continue to be a major source of fertilizer nitrogen.(2,11) Essentially all ammonium nitrate production is based on the reaction of ammonia and nitric acid. As a result, ammonium nitrate production facilities are almost always located adjacent to ammonia plants. More than 40 companies in the United States produce ammonium nitrate, and current production capacity is estimated to be approximately 9,000,000 short tons per year.(11) The locations of major ammonium nitrate plants are shown in Figure 5. More than 85% of the ammonium nitrate produced is consumed in fertilizer applications. Most of the remainder is used in explosives manufacture.

For many years ammonium sulfate was a major source of fertilizer nitrogen in the United States. It still is used in substantial quantities, but production has remained relatively constant for the past 15 years. It is expected that production will remain at approximately the current level in the future. Almost all the ammonium sulfate produced is used in fertilizer applications.

Ammonium sulfate production in the U.S. is based principally on the reaction of ammonia and sulfuric acid. However, by-product sources of ammonia (such as coke oven gas) and sulfuric acid (spent refinery acid) account for a large portion of the ammonium sulfate production. As a result of the use of by-product acid and ammonia there are a large number of relatively small plants producing ammonium sulfate. Many of these are operated by steel companies to utilize the ammonia from coke oven gas. Current production capacity from all sources is estimated to be 3,000,000 short tons of ammonium sulfate per year.(11)

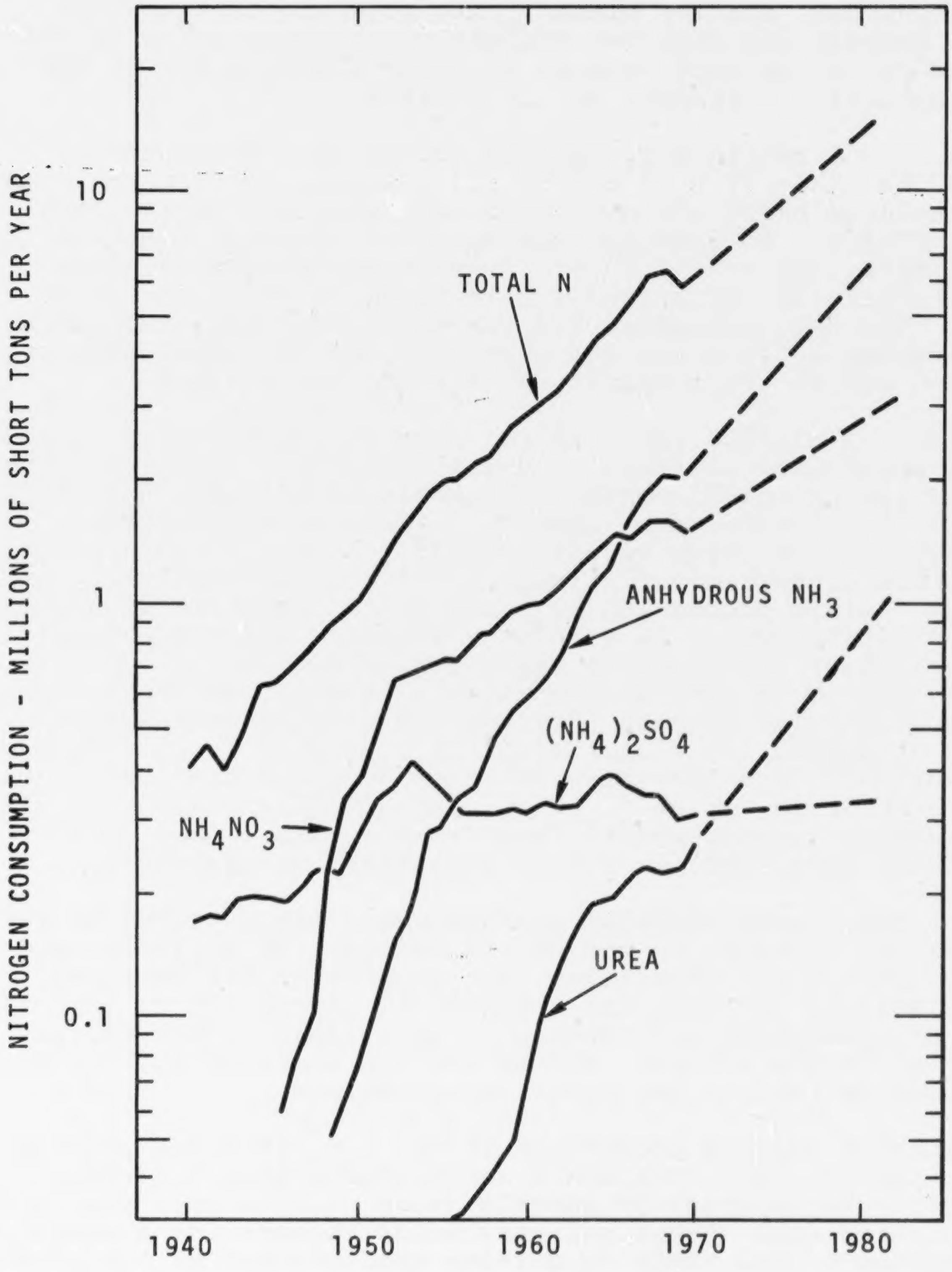


FIGURE 4 CONSUMPTION OF NITROGEN FERTILIZERS IN THE UNITED STATES

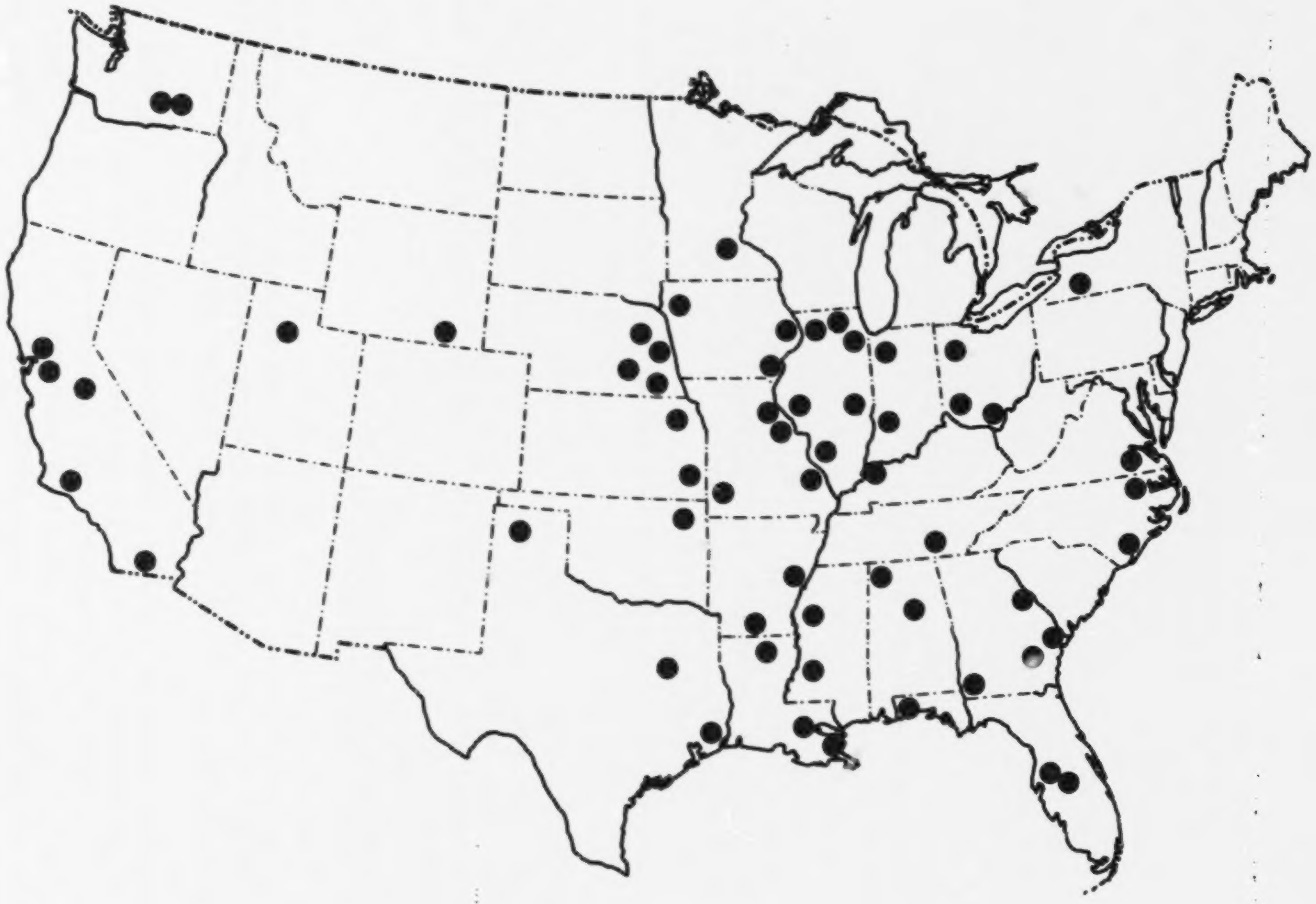


FIGURE 5 LOCATION OF AMMONIUM NITRATE PLANTS IN THE UNITED STATES

The use of urea in fertilizer application is a very recent development. In 1957 only 2% of United States fertilizer nitrogen requirements were supplied by urea. It is estimated that in 1971 this will increase to about 11-12%. Urea production in the United States has increased at an average rate of about 17% a year since 1950. At the present time approximately 75% of the urea produced goes into fertilizer applications, while livestock feeds and urea-formaldehyde resins account for most of the remainder. It is expected that urea consumption in fertilizer applications will continue to grow at a rapid rate in the future, exceeding even the growth rate expected of direct application ammonia.

Principal reasons for the increasing popularity of urea are its high nitrogen content and the absence of hazards in handling and shipping. It has the highest nitrogen content (45%) of any solid fertilizer. These advantages are sufficient to offset the relatively high cost of urea. If urea costs decrease in the future as expected, then it will become even more popular.

All commercial production of urea in the United States is by the reaction of ammonia and carbon dioxide. As a result, urea is almost always produced at an ammonia plant where a supply of ammonia and carbon dioxide is available (carbon dioxide is a by-product of hydrogen production in most ammonia plants). This availability of essentially free carbon dioxide is the principal reason urea production costs are as low as they are. At the present time there are about 35 companies producing urea in the United States. Total production capacity in 1970 was approximately 4,600,000 short tons of urea per year. Production capacities of the larger urea plants range up to 1600 tons per day.(12) Figure 6 gives the location of the major urea plants in the United States.

PHOSPHATE FERTILIZER INDUSTRY

Up until the middle 1950's phosphate was the major fertilizer nutrient consumed in the United States. Since that time nitrogen consumption has become predominant, but phosphates are still used on a very large scale.

The principal source of all phosphate consumed in the United States is phosphate rock. In general phosphate rock has a chemical composition which can be represented by the formula $3Ca_3(PO_4)_2 \cdot CaX_2$ where x may be a halogen, hydroxyl ion, etc. Fluorapatite ($3Ca_3[PO_4]_2 \cdot CaF_2$) is the most prevalent form, and all U.S. phosphate rock contains fluorine in substantial amounts (3-4%).

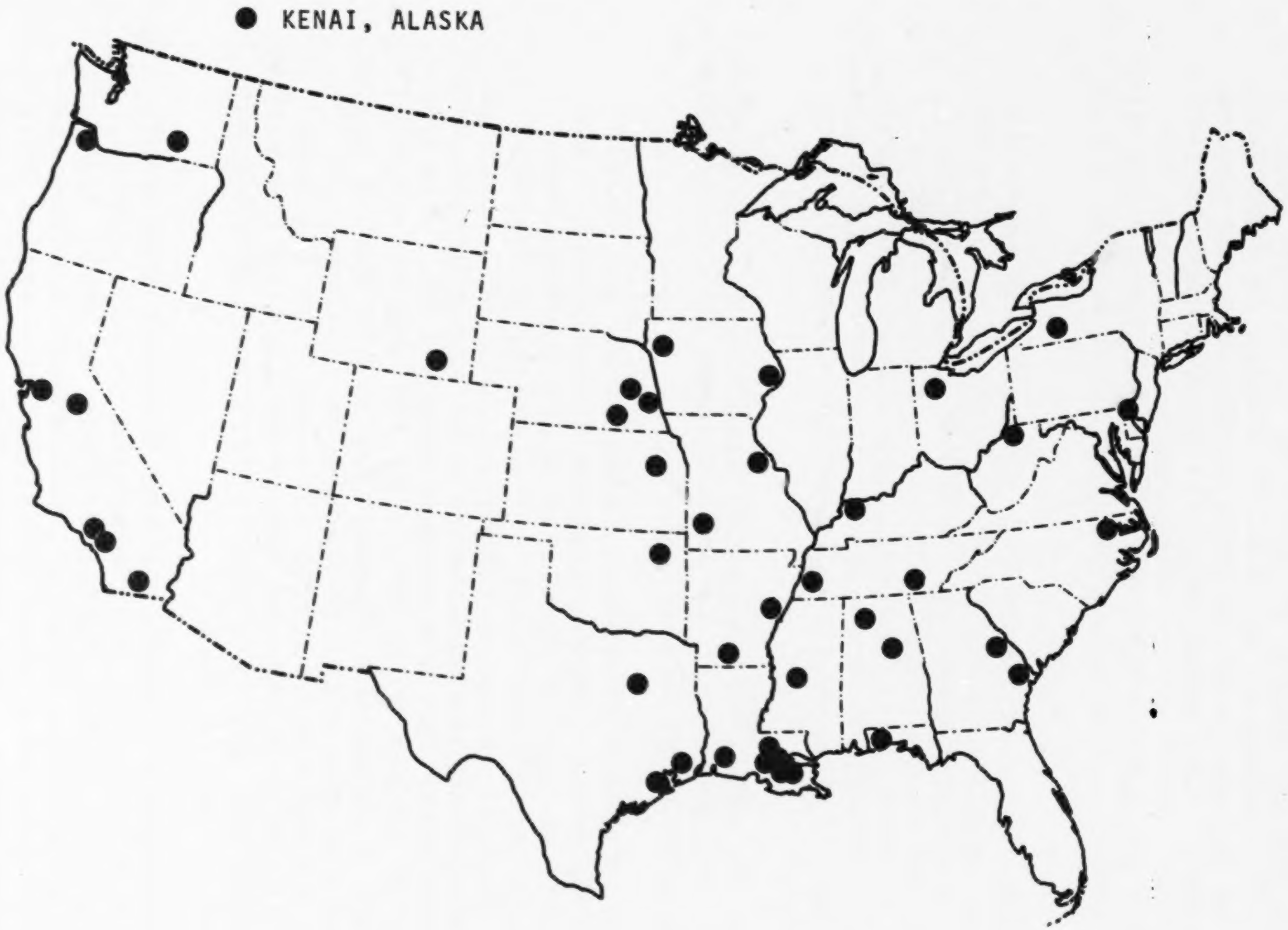

● KENAI, ALASKA

FIGURE 6 LOCATION OF MAJOR UREA PLANTS IN THE UNITED STATES (2)

The phosphate in the rock is almost completely insoluble in soil solutions. In order to be effective in furthering plant growth the phosphate must be soluble to some degree. The basic objective of the phosphate fertilizer industry is to convert the phosphate in the rock to a form that is soluble. The degree of solubility needed is dependent on a number of factors such as soil conditions and degree of fertilization. The water solubility of phosphate fertilizers can vary over a very wide range: from very low solubility for ground phosphate rock to complete solubility. The general trend in the United States is to higher solubility products.

Phosphate rock can be converted to a variety of products for fertilizer applications. Figure 7 shows a schematic diagram of the major fertilizer products obtained from rock. The relative importance of the various products is continually changing and mixed fertilizer--both liquid and solid--are becoming increasingly important. As a result, the direct application of straight phosphate fertilizers is decreasing.

Phosphoric acid, while not consumed directly in any quantity in fertilizer applications, is an indispensable intermediate in phosphate fertilizer production.

The principal straight phosphate fertilizers are triple superphosphate, normal superphosphate and phosphate rock. The major mixed phosphate fertilizers are monoammonium and diammonium phosphates which are normally considered as a single product in presenting production and consumption data. Ammoniated superphosphate is also an important mixed phosphate fertilizer but has no set composition. The composition can be varied by controlling the ammonia-superphosphate ratio. Figure 8 shows the consumption in the United States since 1940 of the principal phosphate fertilizers.(1,2,8) Estimates of consumption through 1980 are also included.(1,2,8) The data presented illustrates very emphatically the strong trend away from low analysis fertilizers such as phosphate rock and normal superphosphates.

Normal superphosphate, which was the dominant source of phosphate for many years, has decreased in consumption since about 1950. Normal superphosphate is still used on a fairly large scale, however, and should continue to be used at a slowly declining but still substantial rate for the next 20 years. All normal superphosphate is produced by the reaction of sulfuric acid and phosphate rock

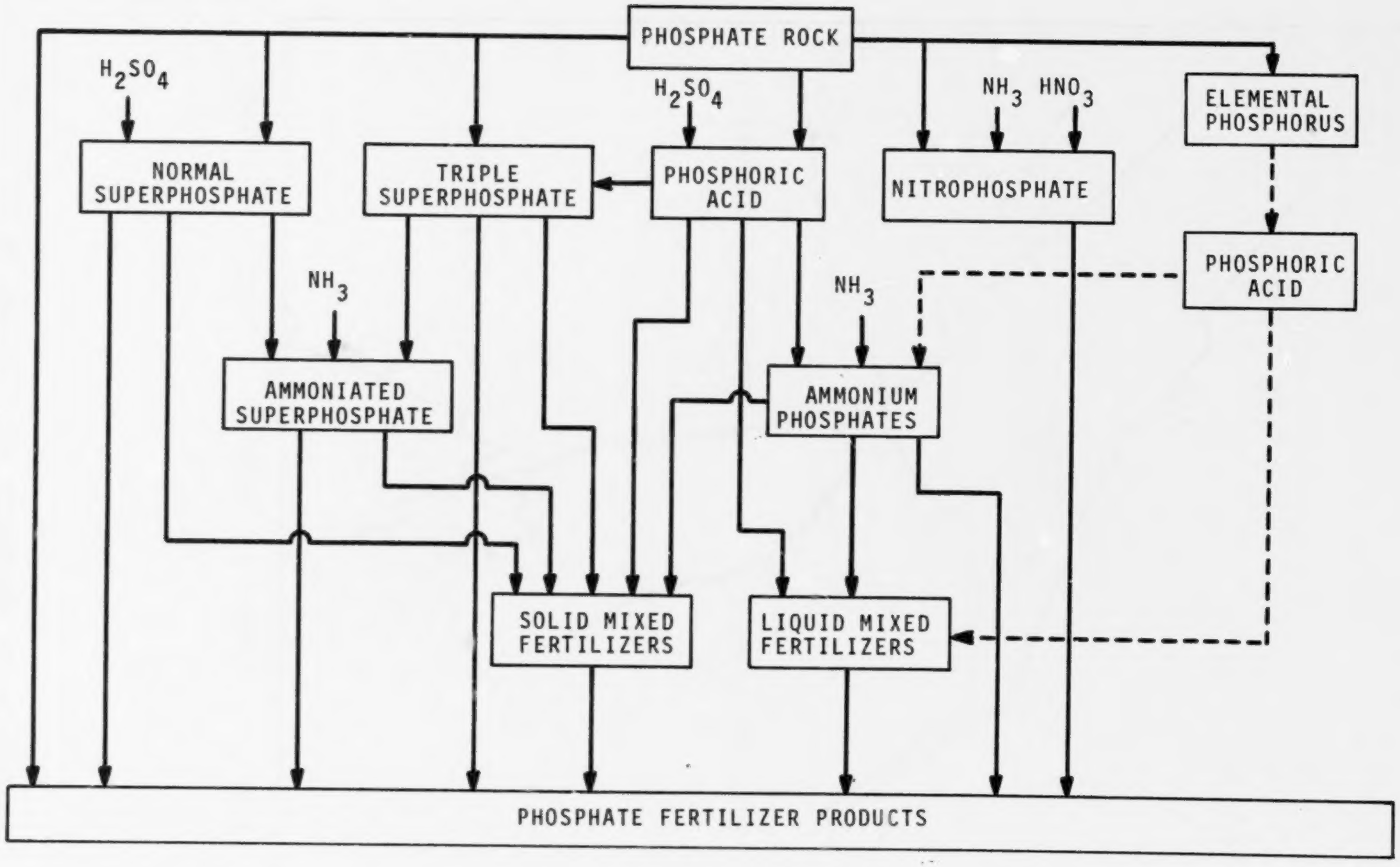

PHOSPHATE ROCK
H_2SO_4
NORMAL SUPERPHOSPHATE
TRIPLE SUPERPHOSPHATE
H_2SO_4
PHOSPHORIC ACID
NH_3 HNO_3
NITROPHOSPHATE
ELEMENTAL PHOSPHORUS
PHOSPHORIC ACID
NH_3
AMMONIATED SUPERPHOSPHATE
NH_3
AMMONIUM PHOSPHATES
SOLID MIXED FERTILIZERS
LIQUID MIXED FERTILIZERS
PHOSPHATE FERTILIZER PRODUCTS

FIGURE 7 FERTILIZER PRODUCTS OBTAINED FROM PHOSPHATE ROCK

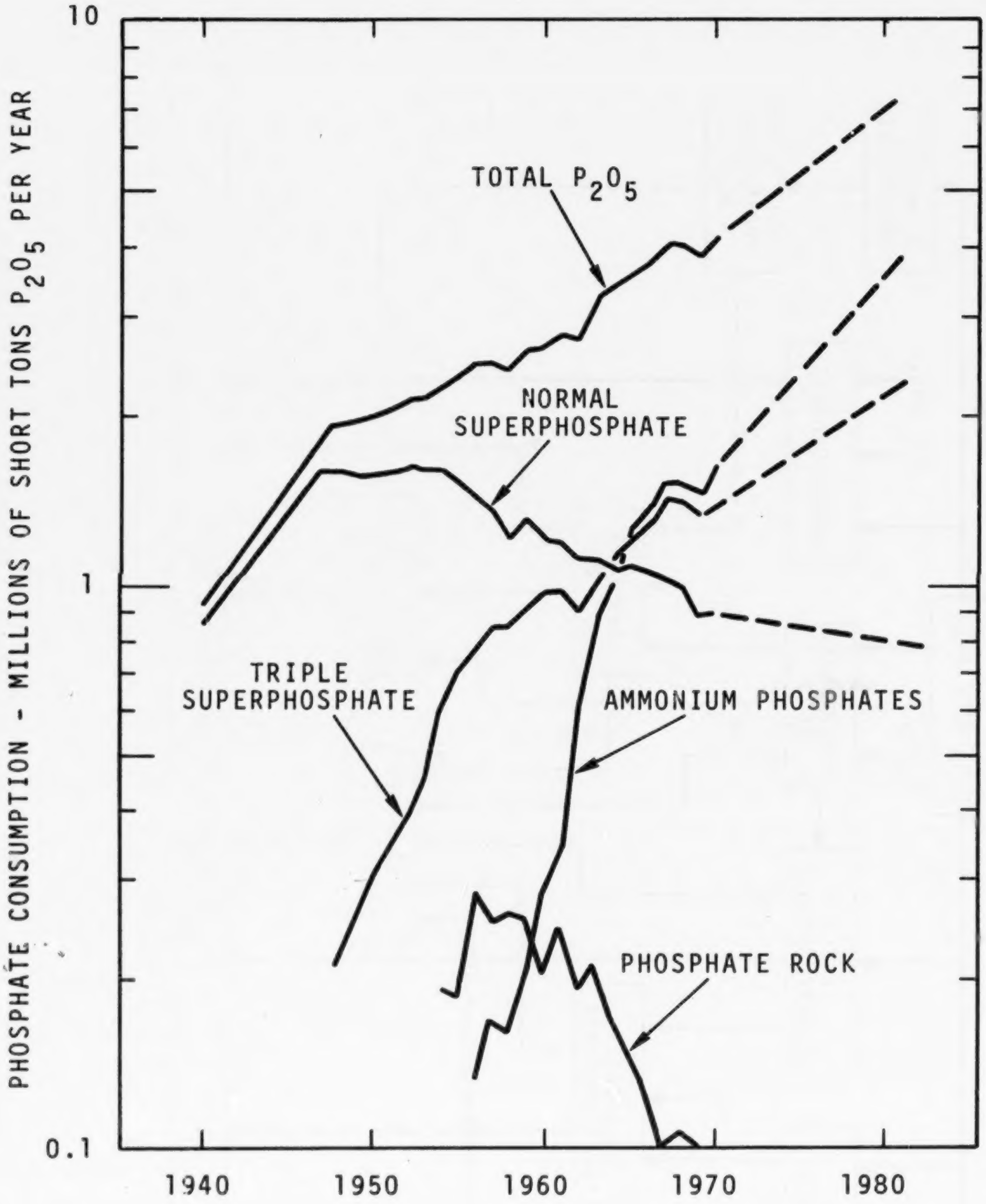


FIGURE 8 CONSUMPTION OF PHOSPHATE FERTILIZERS IN THE UNITED STATES

to give monocalcium phosphate and calcium sulfate. Production plants are relatively small and located at the points of consumption. The low analysis (16-20% P_2O_5) of normal superphosphate makes it cheaper to ship phosphate rock to consumption areas rather than shipping the normal superphosphate from the ore deposits. There are currently about 150 plants producing normal superphosphate in 30 different states. Production capacity in 1969 was estimated to be 4,600,000 short tons normal superphosphate per year, and is expected to drop to 4,500,000 short ton per year in 1974.(11)

Triple superphosphate consumption in the United States has undergone a very rapid growth during the past 30 years. At the present time triple superphosphate is the second leading source of fertilizer phosphate. It is produced by reacting phosphate rock with phosphoric acid to give monocalcium phosphate. Since no calcium sulfate is formed, the P_2O_5 content of triple superphosphate ranges from 44-47%, i.e., about three times that of normal superphosphate. As a result of its high P_2O_5 content, triple superphosphate is usually produced near the phosphate rock deposits and shipped to the market areas for direct application or for use in preparation of mixed fertilizers. There are currently about 20 companies with plants in 10 states producing triple superphosphate. Current productions capacity is estimated to be about 5,800,000 short tons of triple superphosphate per year. About 75% of the production capacity is located in the state of Florida.(11)

The ammonium phosphates have experienced an extremely rapid growth over the past 20 years; they are currently the major source of fertilizer phosphate in the United States. They will probably become even more important in the future. Diammonium phosphate is the preferred form. The ammonium phosphates are produced by reacting phosphoric acid with ammonia. Either wet-process or furnace grade acid can be used, and the product composition can be varied over a wide range by varying the ratio of reactants. Ammonium phosphates are widely used in liquid mixed fertilizers and in combination with other solid fertilizers. It is common practice in many plants to add other fertilizer materials to the phosphoric acid--ammonia reaction to produce solid products of various compositions. Materials which may be added include potassium chloride, sulfuric acid, ammonium nitrate, nitric acid, and urea.

There are more than 40 companies in the United States that produce ammonium phosphates. The locations of the major plants are shown in Figure 9. Current production capacity is approximately 3,800,000 short tons of ammonium phosphates per year.(11)

Ammoniated superphosphate is a major source of fertilizer phosphate in the United States. The name is rather a misnomer since the product usually contains potassium, other nitrogen materials such as ammonium sulfate, and possibly diammonium phosphate. Ammoniated superphosphate is normally produced by reacting normal or triple superphosphate with an ammoniating solution to form calcium phosphate and monoammonium phosphate. The ammoniating solution is an aqueous solution of ammonia, ammonium nitrate, and possibly urea. The solution composition can vary over a wide range depending on the product desired. Current practice favors production of a granular material. As a result, ammoniated superphosphate production has been closely related to the development of granulation techniques. Many different granular fertilizer formulations can be prepared, based on the ammoniation of superphosphate, by adding other fertilizer materials to the reaction mixture. The materials that may be added include anhydrous ammonia, ammonium sulfate, diammonium phosphates, phosphoric acid, sulfuric acid, and potassium chloride.

With the increased use of high analysis fertilizers, phosphoric acid becomes increasingly important in the phosphate fertilizer industry. Phosphoric acid is produced by two basic processes. In the wet process, phosphate rock is reacted with a strong mineral acid (usually sulfuric) to form orthophosphoric acid. In the furnace process phosphate rock is converted to elemental phosphorous which is burned to P_2O_5 and then reacted with water to form the acid. Both wet-process and furnace grade phosphoric acid are used in the fertilizer industry. However, the tonnages of furnace grade acid consumed are relatively small. Figure 10 shows the production of both types of acid in the United States since 1940. Most furnace grade acid is used in nonfertilizer applications, but its use in the fertilizer industry should increase in the future. Almost all of the wet-process phosphoric acid produced in the United States is used by the fertilizer industry. Total phosphoric acid production should experience the same growth in the future that is predicted for the phosphate fertilizer industry. Because of the uncertainty of the future of phosphates in the detergent industry it is difficult to predict the future of furnace grade acid. However, it will probably continue to grow at a modest rate.

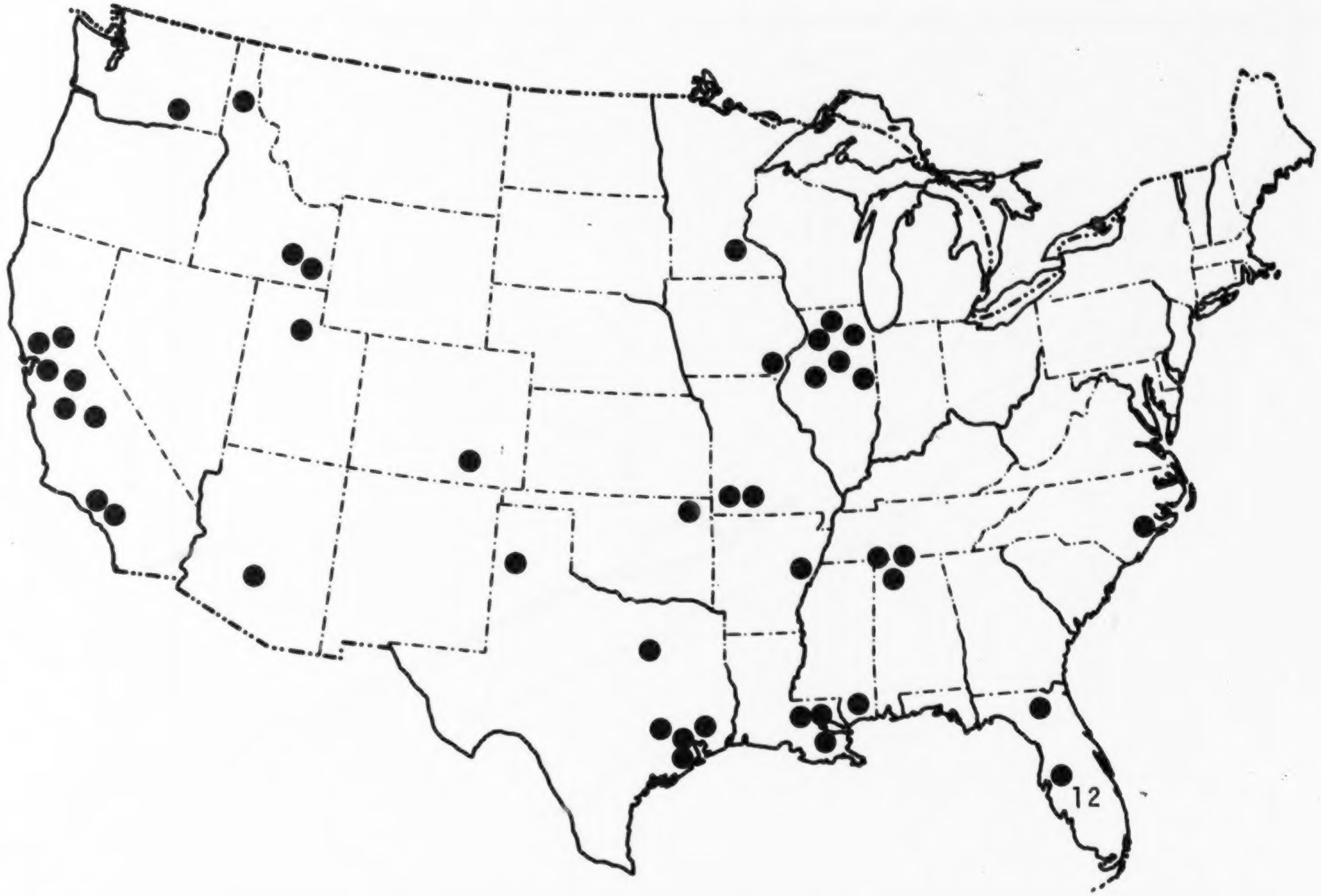


FIGURE 9 LOCATION OF MAJOR AMMONIUM PHOSPHATE PLANTS IN THE UNITED STATES (11)

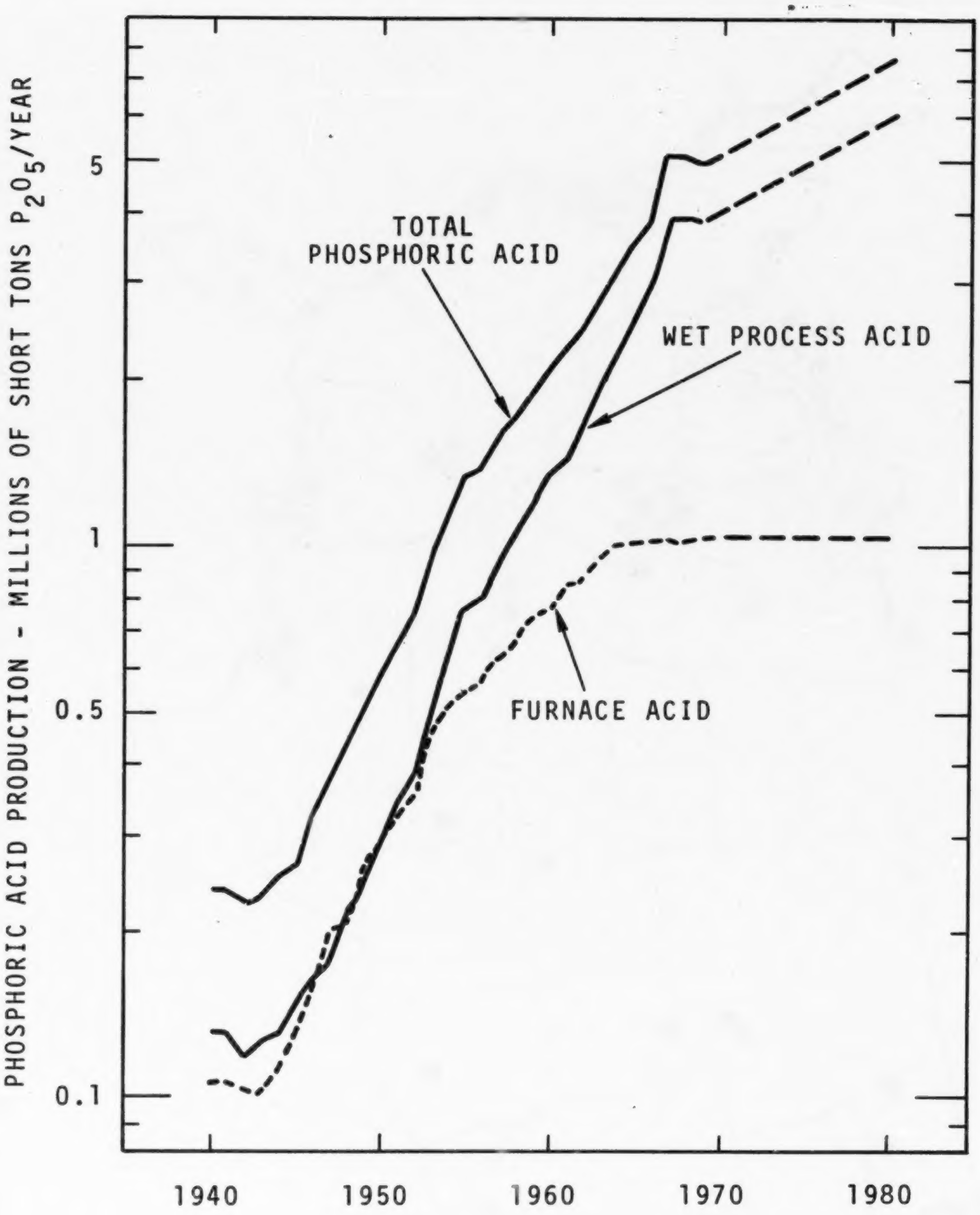


FIGURE 10 PHOSPHORIC ACID PRODUCTION IN THE UNITED STATES

At present there are about 35 companies producing wet process phosphoric acid in the United States and 8 companies (including TVA) producing furnace acid. Figure 11 shows the location of the major phosphoric acid plants in the United States. Wet process acid production capacity in 1969 was estimated to be 5,800,000 short tons P_2O_5 per year; furnace grade acid capacity was 1,700,000 short tons P_2O_5 per year.(11)

POTASH INDUSTRY

Potassium is one of the three primary nutrients required for plant growth. The functions of potassium in the plant growth cycle are not well defined. However, it is required in relatively large amounts to assure healthy plant growth. In most cases plant requirements for potassium exceed those for phosphorus and sometimes approach the requirements for nitrogen.(9) Thus, potassium is used in large quantities in fertilizer applications throughout the world.

In the potassium (and fertilizer) industry the term "potash" is normally used to refer to any potassium compound which is used for its potassium content. Regardless of the source of the potassium, it is fertilizer industry practice to state the potassium content of the compound in terms of its equivalent potassium oxide (K_2O) content. Pure potassium chloride, for example, has an equivalent K_2O content of 63.17%. The K_2O content of other common potassium compounds is given below.

Pure Compound	Equivalent K_2O Content (%)
KNO_3	46.6
K_2SO_4	54.1
K_2CO_3	68.2
$KHCO_3$	47.0
KOH	83.9
KOH (45% Solution)	37.8
KCl	63.2

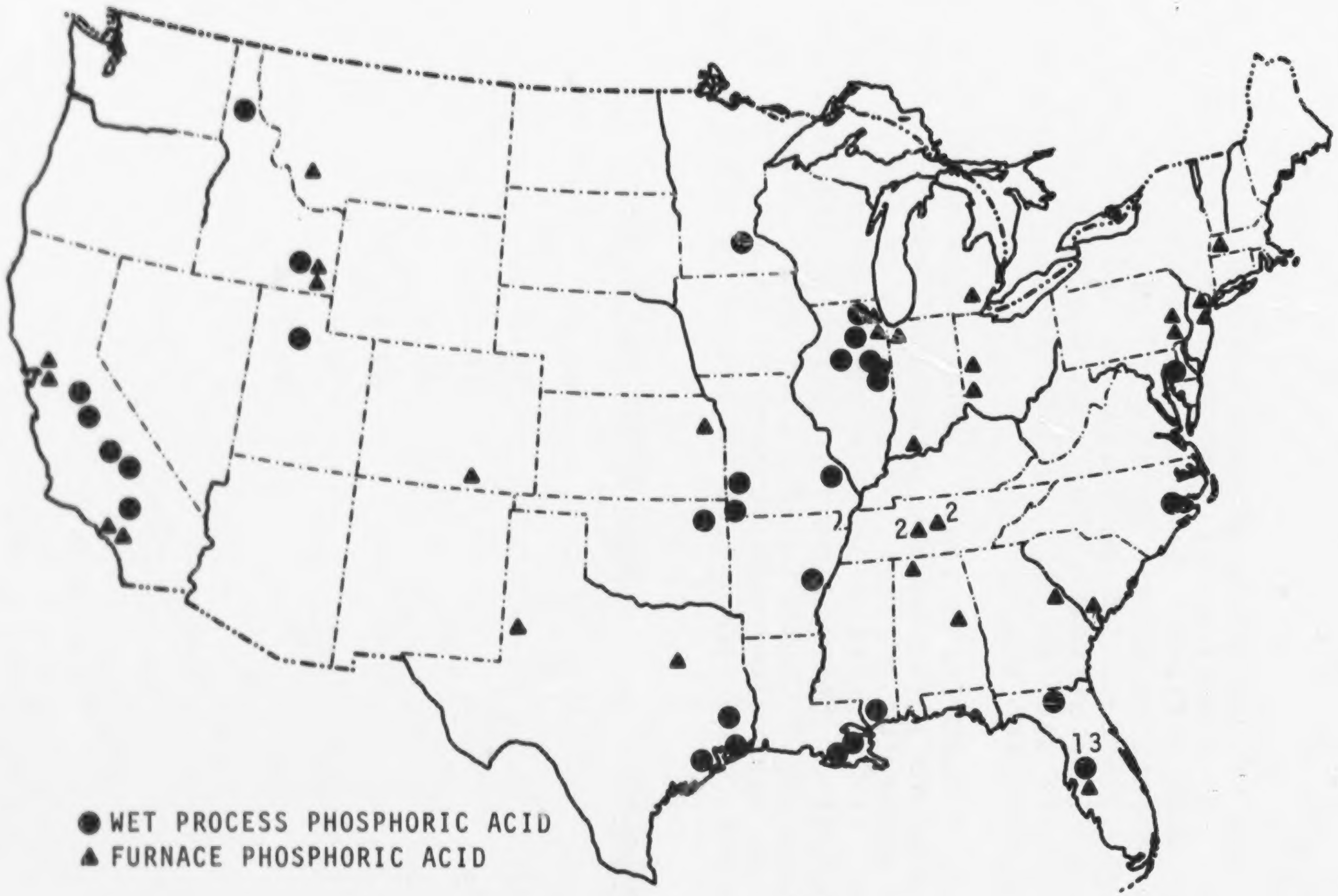

2
2
13
● WET PROCESS PHOSPHORIC ACID
▲ FURNACE PHOSPHORIC ACID

FIGURE 11 LOCATION OF MAJOR PHOSPHORIC ACID PLANTS IN THE UNITED STATES (11)

More than 90% of the potash consumed in the United States each year goes into fertilizer applications. As a result, the potash industry has experienced the same rapid growth over the past 30 years which other segments of the fertilizer industry have known. Data presented in Figure 12 illustrate the rapid growth of potash production and consumption in the United States since 1940. The relatively depressed state of the U.S. fertilizer industry has held potash production and consumption relatively constant since 1967. However, long range projections show that potash consumption (primarily in the fertilizer industry) should grow at a substantial rate between 1970 and 1980.(2) The rate of growth will probably be somewhere between the rates experienced by the nitrogen and phosphorus based fertilizers.

Potassium chloride is the major source of the fertilizer potassium consumed in the United States. It normally accounts for 90-95% of the potash used in fertilizer applications. The popularity of KCl is the result of its ready availability, low price, and high K_2O content. Potassium sulfate supplies most of the remaining potash requirements of the fertilizer industry (5-6%). Potassium nitrate, potassium hydroxide, potassium magnesium sulfate, and the potassium phosphates are also used in fertilizer applications, but only to a very limited extent.

Direct application of fertilizer potash is relatively limited, and accounts for only about 22% of the potash used in the U.S. in fertilizer applications.(2,9) The bulk of the potash is used in either blended solid fertilizers or liquid fertilizers. The direct application of potash is growing, however, since plant requirements for potash can be satisfied by relatively infrequent applications.

The major sources of potash in the United States are the sylvinite deposits in New Mexico and Utah and the natural brines at Searles Lake, California, and Bonneville, Utah. Sylvinite, a physical mixture of halite (NaCl) and Sylvite (KCl), accounts for about 90% of U.S. potash production. There are currently 10 major potash producers in the United States, seven of which operate in the Carlsbad area of New Mexico (see Figure 13). Production capacity of the 10 producers is reported to be approximately 3.8 million short tons K_2O/year.(2) The New Mexico operations produce the bulk of U.S. potash output (approximately 80%). The high grade ores in New Mexico are being slowly depleted, however, and there is considerable interest developing in the sylvinite deposits in eastern Utah. In addition, Canadian production of potash will have a significant effect on future potash developments in the United States.

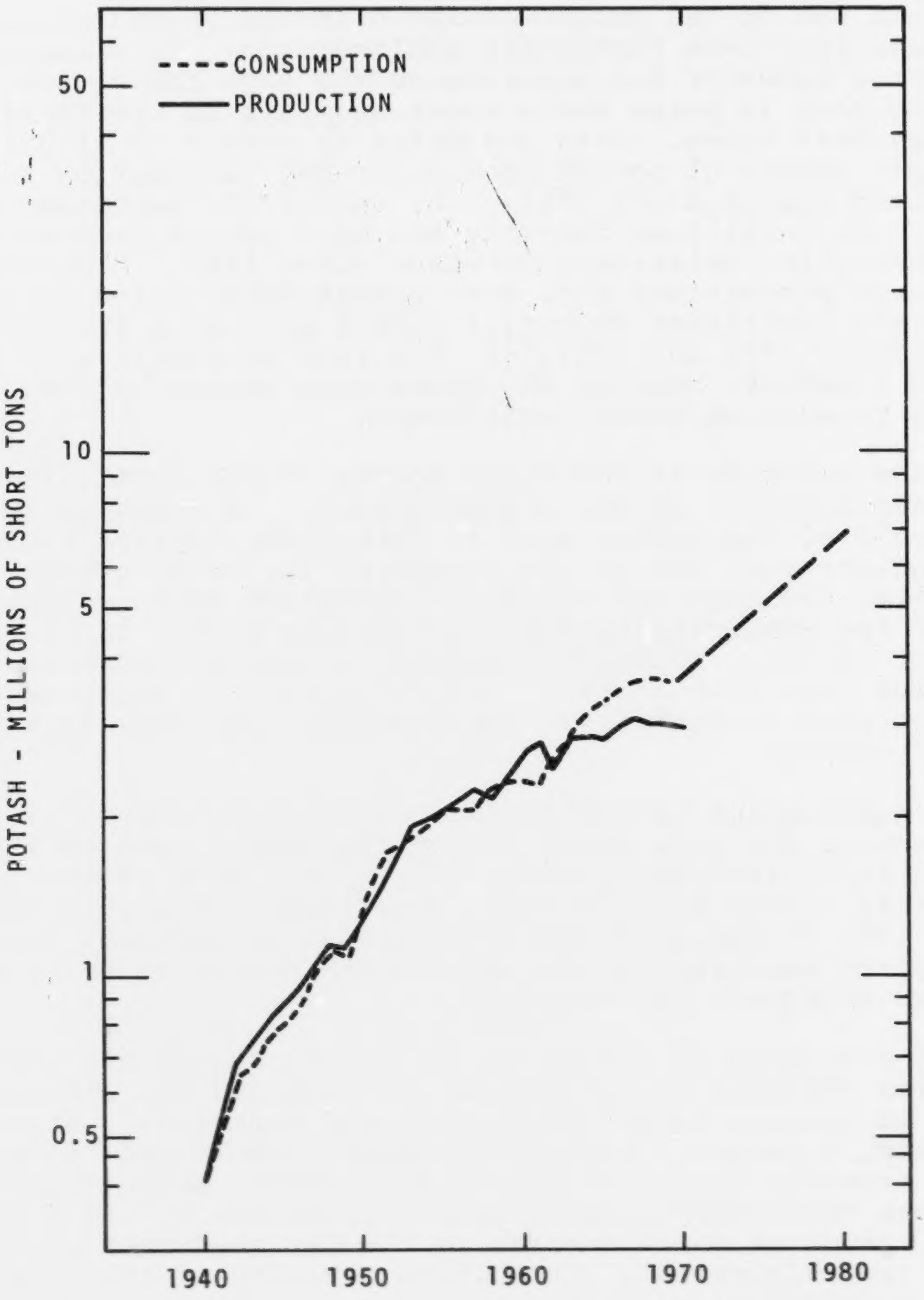


FIGURE 12 POTASH PRODUCTION AND CONSUMPTION IN THE UNITED STATES

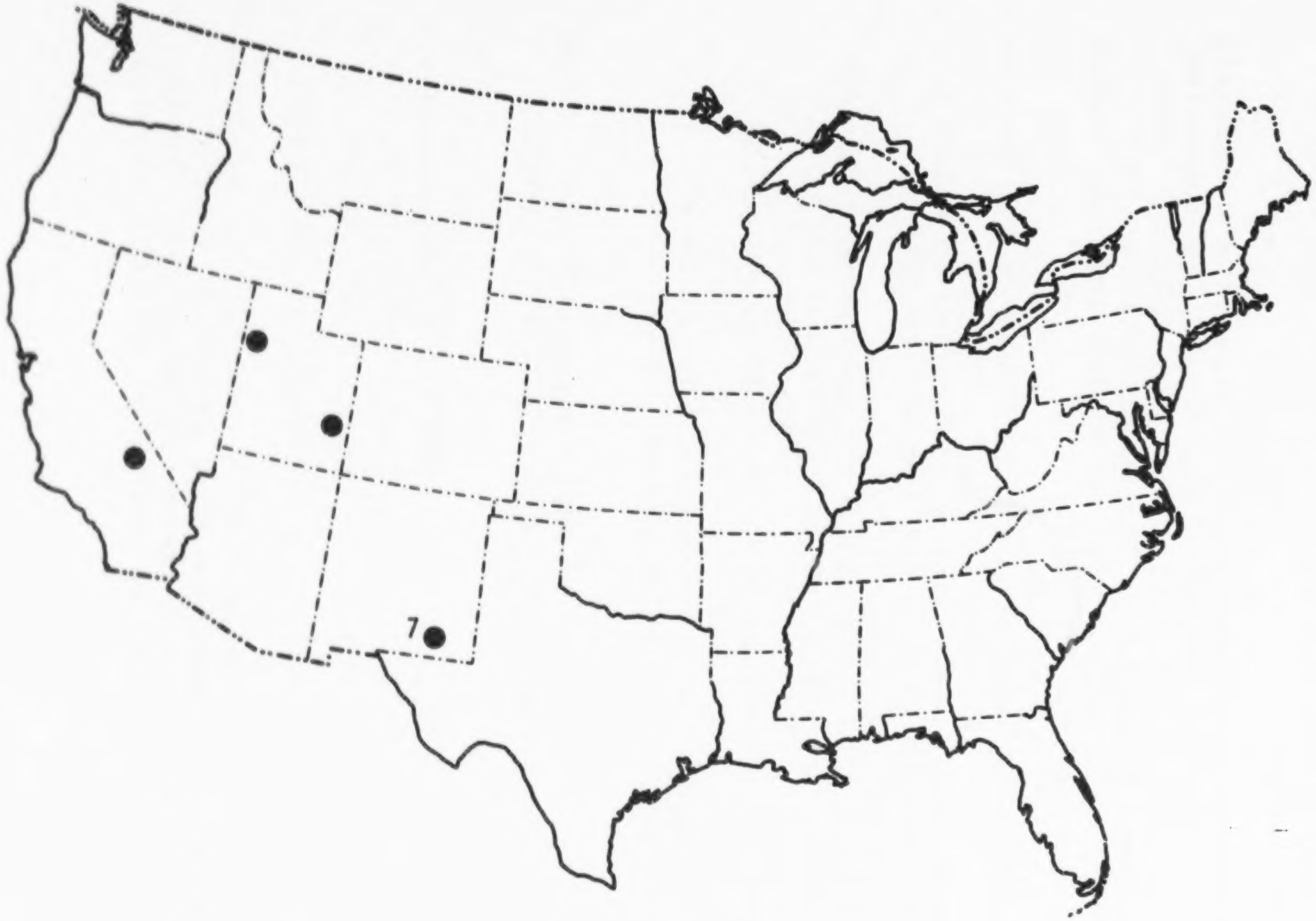


FIGURE 13 LOCATION OF POTASH PRODUCERS IN THE UNITED STATES

With current annual U.S. consumption of potash being approximately 3 million short tons of K_2O, there is considerable overcapacity in the United States. A recent Bureau of Mines report(13) estimates that the domestic demand for potash will not catch up with the overcapacity until 1974 and possible much later. The Bureau also estimates that Canadian producers will supply the bulk of U.S. potash requirements for the next few years.

Recovery of potassium chloride from sylvinite is a relatively simple operation. The ore is mined and the KCl is separated from the NaCl and gangue material. No major chemical operations are involved. Potassium chloride production from sylvinite is, therefore, essentially a mining industry rather than a chemical processing industry.

Underground deposits of sylvinite can be mined in two ways:

1. By traditional shaft mining techniques in which a shaft is sunk to the ore bed and crushed ore hauled to the surface.
2. By solution mining in which the potassium chloride is dissolved in-situ and raised to the surface in solution form. At the present time only shaft mining for potash recovery from sylvinite is practiced in the United States. There is talk in the industry, however, that at least one U.S. producer is considering solution mining.

Various grades of KCl are used in the potash industry. Grading is based on purity and particle size. Current purity designations(2) are as follows:

Grade	Purity	Major End Use
fertilizer	95-97% KCl	Solid Fertilizers
soluble	99% KCl	Liquid Fertilizers
chemical	99.95% KCl	Industrial Chemicals

The use of KCl in blended solid fertilizers has placed certain restrictions on particle size and most producers supply the various grades of KCl in different size ranges. Typically, a specific grade of KCl would be available in the following size grades.(2)

Grade	Size Range
standard	100% - 20 mesh
	95% + 65 mesh
coarse	100% - 14 mesh
	95% + 28 mesh
granular	100% - 6 mesh
	98% + 20 mesh

Two basic types of processes are being used by U.S. producers to recover KCl from sylvinite ore: flotation beneficiation, and solution-recrystallization. Flotation beneficiation produces a fertilizer-grade KCl for use in solid fertilizers. Solution-recrystallization normally produces a soluble-grade KCl for use in liquid fertilizers.

In the typical flotation process sylvinite ore is crushed, then pulped with saturated brine of KCl and NaCl, clay slimes and insoluble ore removed, and then the KCl and NaCl are separated by flotation. The KCl produced contains NaCl and small amounts of clay and iron. About 65-70% of U.S. sylvinite production is processed by flotation.

The solution-recrystallization process is based on the facts that KCl is much more soluble in hot water than in cold, while NaCl is only slightly more soluble in hot water than cold. Typically, ground sylvinite ore is treated with a heated recycle KCl-NaCl brine. The KCl goes into solution together with a small amount of NaCl. Solids are removed from the solution and then it goes to crystallizers where it is cooled to drop out the KCl. The KCl is recovered by filtration and then washed and dried. The brine solution is recycled, after heating, back to the dissolution operation.

Gravity separation can also be used to produce a crude grade of KCl from sylvinite. In this process the ore is first crushed and screened. The screened ore is then mixed with a saturated solution of NaCl and KCl and sent to a bank of Wilfley tables where the KCl and NaCl crystals are separated by gravity difference. The KCl product contains approximately 50% K_2O equivalent.

Recovery of KCl from natural brines is a much more complex process than recovery from sylvinite. The Searles Lake brine is a complex mixture of sodium and potassium salts. The salt bed is divided into two layers and the typical composition of brine from each layer is given below.(14)

Major Components	Upper Layer	Lower Layer
KCl	5.02%	2.94%
NaCl	16.06	15.51
Na_2SO_4	6.75	6.56
Na_2CO_3	4.80	6.78
$Na_2B_4O_7$	1.63	1.90
KBr	0.12	0.08

The potassium is recovered primarily from the upper layer and involves a large number of carefully controlled operations to produce a high purity KCl product.

The Bonneville (Salduro Marsh) brines are a complex mixture of metal chlorides and sulfates. A typical brine composition is shown below.(14)

Component	Percent
NaCl	18.0 - 24.0
KCl	0.8 - 1.2
$MgCl_2$	0.9 - 1.2
$MgSO_4$	0.2 - 0.3
$CaSO_4$	0.3 - 0.4
LiCl	0.03- 0.04

The brine is first concentrated in ponds by solar evaporation until it is saturated with KCl. The brine is then pumped to a second series of ponds where it is evaporated to deposit a mixture of KCl and NaCl. Concentration is continued until carnallite ($KCl \cdot MgCl_2$) begins to precipitate. The brine is then removed from the ponds and the KCl-NaCl mixture collected and sent to the refinery. At the refinery the KCl-NaCl mixture is separated by flotation beneficiation to give a fertilizer grade KCl.

Because of the widespread use of KCl in different types and grades of solid mixed fertilizers, there has been an increasing demand for KCl of larger particles than is readily obtained from the normal production methods. This has led to the development of methods for increasing the particle size of fertilizer grade KCl. Both compaction and fusion techniques are being used. In the fusion process(14) finely divided KCl is melted and then solidified in thin layers. The layers are crushed and screened to give the desired particle size. Undersize particles are recycled. In the compaction process(14) the finely divided KCl is compacted into thin sheets using high pressure rolls at 200-250 °F. The KCl sheet is then flaked, crushed, and screened.

WATER USE IN THE FERTILIZER INDUSTRY

There is very little information in the literature on the overall water requirements of the entire fertilizer industry. There are references to water consumption for specific plants or processes but none that cover the entire industry. Census of Manufacturers publications by the United States Department of Commerce(15) have reported water use patterns for SIC 2871 (Fertilizers). However, this data does not include water used in the production of ammonia, urea, phosphoric acid and phosphate rock, all of which are large consumers of water. The Census of Manufacturers data for SIC 2871 are plotted in Figure 14. Figures on water use for SIC 28 (Chemicals and Allied Products) which includes all of the fertilizer materials of interest except phosphate rock, are also included. The data show that water use in the fertilizer industry is growing at a faster rate than for the chemical industry as a whole. This reflects the rapid growth of fertilizer production since 1954.

In the present study a total of 33 fertilizer producers throughout the country have supplied information on the water required in the production of various fertilizer materials and intermediates. Data on both gross and intake water requirements were obtained. Table 3 summarizes the data on gross water requirements. There is a considerable range in water requirements for production of a given material. This is due to a number of factors including processing alternatives, water availability, and air pollution control which can require considerable water scrubbing of gas streams. For example, in the production of materials such as the superphosphates, ammonium phosphates, ammoniated superphosphate, and granular N-P-K fertilizer water requirements were reported to vary from 0-15,000 gallons per ton of product. This range is due primarily to varying requirements for water scrubbing of gaseous effluents. In urea production the wide range in water requirements reflects the type of process used -whether once-through, partial recycle or total recycle.

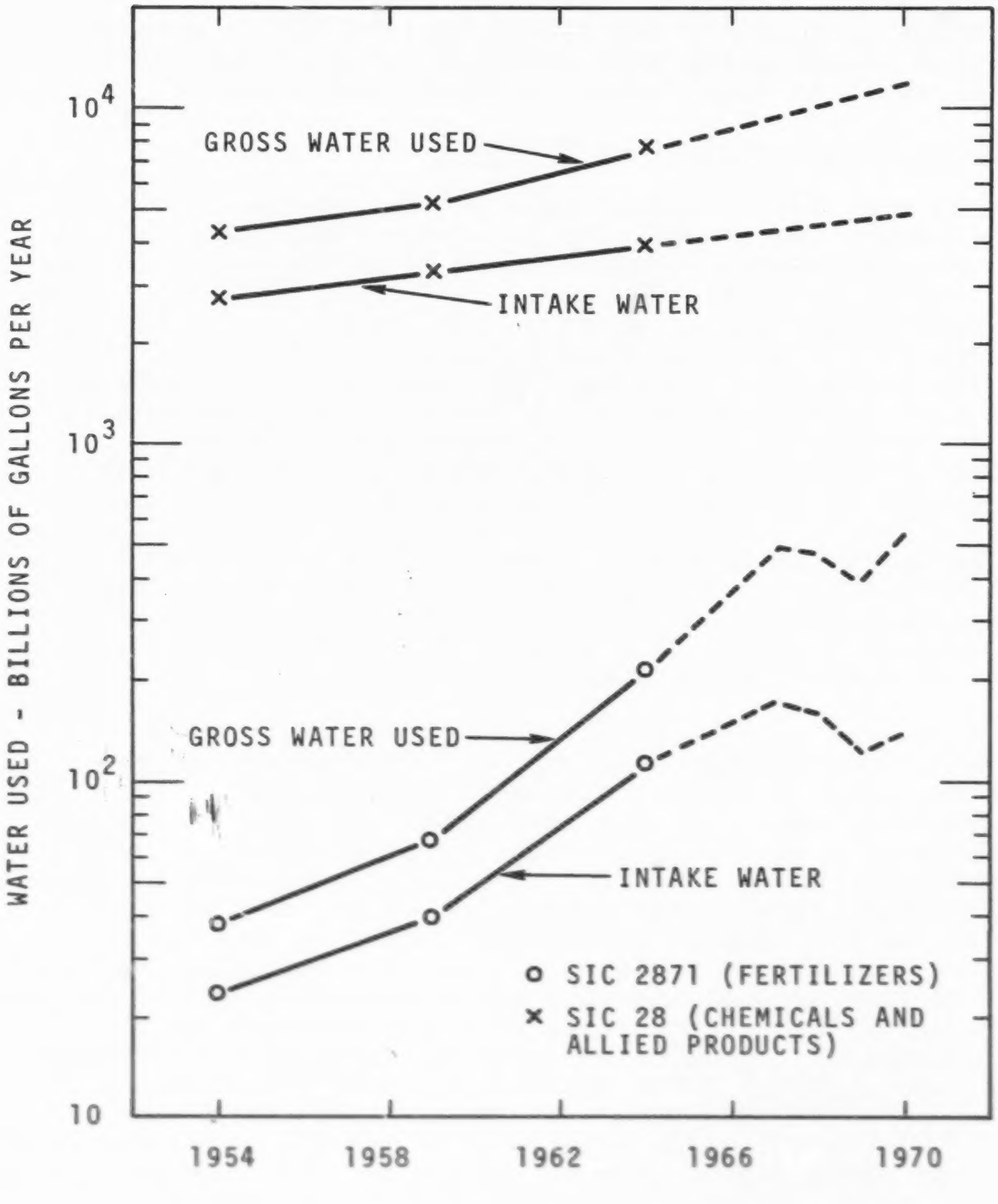


FIGURE 14 WATER USE BY THE FERTILIZER INDUSTRY - SIC 2871 (15)

TABLE 3

WATER REQUIREMENTS FOR PRODUCTION OF VARIOUS FERTILIZERS*

Fertilizer Product	Gross Water Requirements
Ammonia	56,000-188,000 gal/ton NH_3
Ammonium Nitrate	3,000-35,000 gal/ton NH_4NO_3
Ammonium Sulfate	100-10,000 gal/ton $(NH_4)_2SO_4$
Urea	20,000-90,000 gal/ton urea
Phosphoric Acid (wet process)	20,000-40,000 gal/ton P_2O_5
Phosphoric Acid (furnace)	32,000-50,000 gal/ton P_2O_5
Normal Superphosphate	0-3,000 gal/ton Product
Triple Superphosphate	0-5,000 gal/ton Product
Ammonium Phosphate	0-15,000 gal/ton Product
Ammoniated Superphosphate (Granular N-P-K Fertilizers)	0-5,000 gal/ton Product
Potassium Chloride	20,000-40,000 gal/ton KCl

*Information supplied by numerous fertilizer producers throughout the United States.

Using the data presented in Table 3 and knowing the yearly production rates for each fertilizer material, one can obtain a rough estimate of water use by the fertilizer industry (water used in fertilizer blending plants and in production of minor products is quite small and should not contribute significantly to overall water consumption by the industry). Such an estimate has been made, using an average water consumption figure for each product, and the results are shown in Figure 15. Estimated water consumption beyond 1970 is based on estimated fertilizer production and current water use rates. The estimates of water consumption are significantly higher, over corresponding periods, than those reported by the Census of Manufacturers. This reflects the large volume of water used in ammonia, urea, phosphoric acid and elemental phosphorus production.

Water reuse patterns vary significnatly from material to material and from plant to plant. Some companies reported essentially once-through use of water, while others reported complete recycle and entirely closed loop operation. At the current time, based on information from the 33 companies, water recycle accounts for 75-80% of the gross water requirements of the fertilizer industry. As water pollution control standards become more stringent, water recycle should increase. This is substantiated by Census of Manufacturers data which show that water reuse for SIC 2871 (fertilizers) increased from 40 to 48% between 1958 and 1964. This compares with estimates of 75-80% water recycle for 1970 for the entire fertilizer industry.

The major portion of the water used by the fertilizer industry is for cooling purposes. In 1964 it was reported that 53% of the water used was for cooling. However, based on information obtained in the current study cooling water accounted for between 70-80% of all water usage.

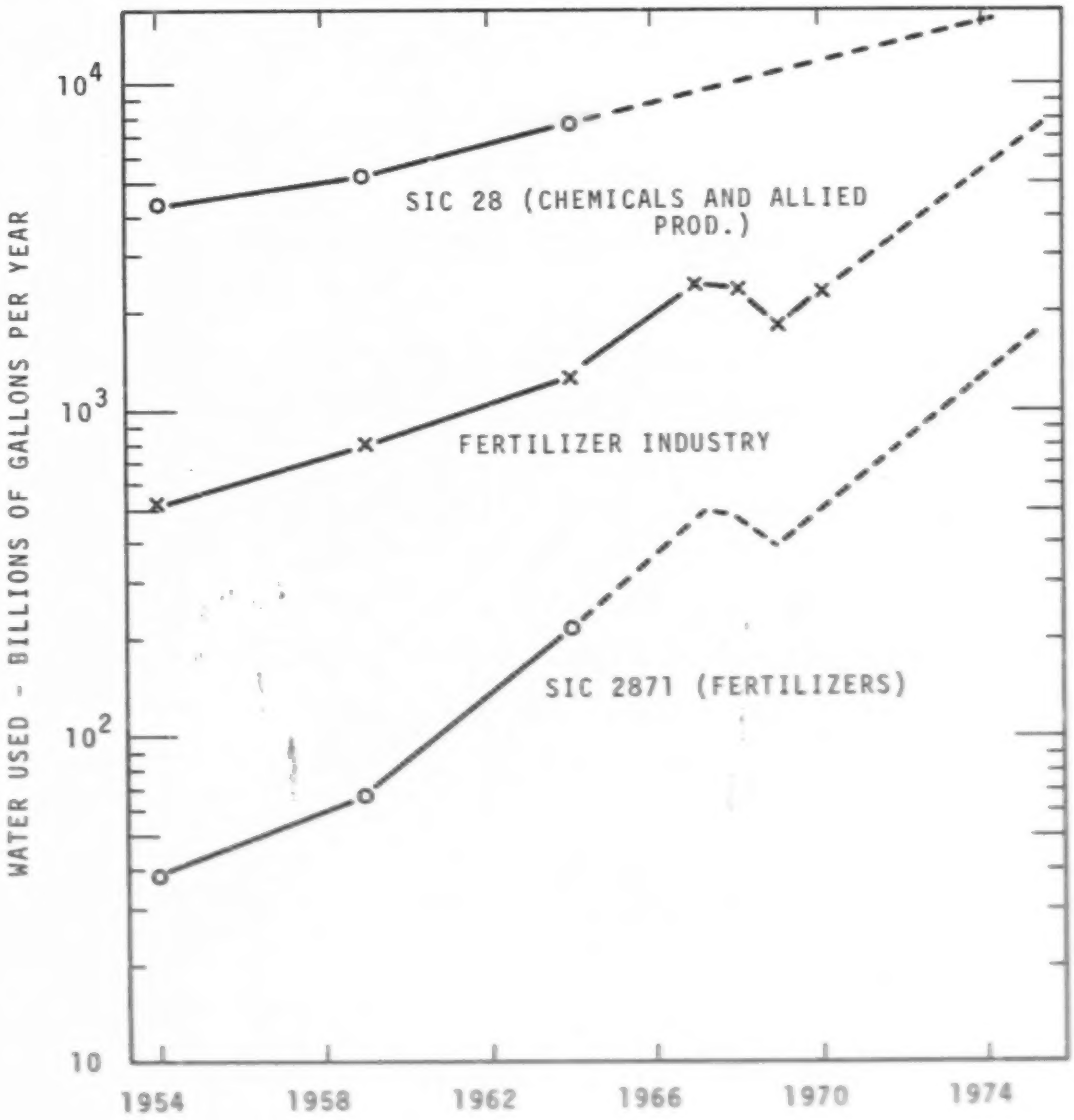


FIGURE 15 ESTIMATED WATER USE BY THE ENTIRE FERTILIZER INDUSTRY (Based on information obtained in current study)

Almost all of the ammonia is produced by the direct reaction of nitrogen and hydrogen (Haber-Bosch process) in a converter. The reaction is

$$N_2 + 3\ H_2 \rightarrow 2\ NH_3$$

This reaction is exothermic and care must be taken to control the temperature in the converter. The conversion to ammonia is low (10-20%) and the standard practice is to condense the ammonia from the gas stream and recycle the unreacted nitrogen and hydrogen. Increasing the reaction pressure increases the ammonia conversion and most ammonia plants operate the converter in the range of 120-700 atmospheres pressure.(16,17,18) Increasing the reaction temperature decreases the ammonia concentration at equilibrium. However, increasing the temperature increases the rate of ammonia formation so it is necessary to select a convertor temperature which gives maximum ammonia production. Most convertors operate in the range of 400-600 °C.(16,17,18)

The rate of reaction between nitrogen and hydrogen is very slow regardless of temperature. Economic production of ammonia, therefore, requires a catalyst to accelerate the reaction rate to a useful level. The catalyst used is iron promoted with metal oxides such as CaO, Al_2O_3, MgO, K_2O, and SiO_2 (each catalyst manufacturer has his own formula). Effective catalyst life is dependent on a number of factors and excessive temperature is especially damaging. Therefore, careful control of the temperature in the reactor must be maintained to obtain an optimum balance of ammonia production and catalyst life. Impurities in the feed gas can also have a harmful effect on the catalyst. Sulfur, chlorine and oxygen containing compounds must all be removed from the feed to insure efficient catalyst operation.

A major factor in ammonia synthesis is the preparation of the feed gas. Atmospheric nitrogen is readily available and is always the nitrogen source used. Obtaining the hydrogen is always the major problem in an ammonia plant. A number of different hydrogen sources have been used, including coke oven gas, refinery gas, naphtha, fuel oil, crude oil, and electrolytic hydrogen. In the United States at the present time most of the hydrogen used in ammonia production comes from natural gas.

There are four major steps in preparing the hydrogen from natural gas: (1) removal of sulfur impurities; (2) reaction of the gas with oxygen to form hydrogen and carbon monoxide; (3) conversion of the carbon monoxide to carbon dioxide; and (4) removal of the carbon dioxide and residual carbon monoxide from the hydrogen. In most cases the sulfur compounds are removed from the natural gas by the gas producer. If additional sulfur removal is required then the ammonia producer can use ethanolamine, iron oxide, or activated carbon to reduce the sulfur to the required level.

Several processes have been developed for converting the natural gas to hydrogen and carbon monoxide. In the United States, steam reforming and noncatalytic partial oxidation are the most widely used processes. Approximately 65% of U.S. ammonia production uses steam reforming of natural gas. In the steam reforming process, natural gas and steam are reacted over a nickel catalyst at 1200-1300 °C in a primary reformer to form carbon monoxide and hydrogen. The reaction is

$$C_xH_y + x\ H_2O \rightarrow x\ CO + (x + \frac{y}{2})\ H_2$$

The reaction is only partially completed in the primary reformer. A secondary reformer is used to convert the remaining hydrocarbon. Air is injected into the secondary reformer to burn unreacted hydrocarbon and hydrogen and to supply heat. The air used is sufficient to give a hydrogen-to-nitrogen ratio of 3:1 in the product gas stream. The gas from the secondary reformer contains hydrogen, carbon monoxide, nitrogen, steam, and small amounts of carbon dioxide, argon, and unreacted hydrocarbon.

In the noncatalytic partial oxidation process the hydrocarbon feed and oxygen, or oxygen-enriched air, are preheated separately and then reacted at about 1400 °C and 30 atmospheres pressure to form carbon monoxide and hydrogen:

$$C_xH_y + \frac{x}{2}\ O_2 \rightarrow x\ CO + \frac{y}{2}\ H_2$$

The product gas stream contains hydrogen, carbon monoxide, carbon dioxide, and small amounts of nitrogen, unreacted hydrocarbon, and argon. The oxygen for the reaction is obtained from a liquid air plant. The nitrogen from the liquid air plant serves as the nitrogen supply for the synthesis reaction.

The oxides of carbon must be removed from the synthesis gas before it goes to the converter. First step in the purification of the synthesis gas is the shift conversion of carbon monoxide to carbon dioxide. This is accomplished by reacting the carbon monoxide with steam over an iron oxide-chromium oxide catalyst:

$$CO + H_2O \rightarrow H_2 + CO_2$$

The reaction, which is exothermic, is usually carried out in a series of converters at a temperature of about 400 °C using an excess of steam. The degree of conversion desired depends on the process which is used to remove the carbon dioxide from the synthesis gas. It is usually preferable to reduce the carbon monoxide to less than 0.5%.

Several methods have been developed for removing the carbon dioxide from the synthesis gas. In the United States monoethanolamine (MEA) scrubbing is the preferred process. By scrubbing the synthesis gas with a 30% MEA solution, it is possible to reduce the CO_2 content of the gas to less than 0.5%. The CO_2 is stripped from the MEA solutions and the solution is recycled. The CO_2 is discharged to the atmosphere, or can be used in other processes such as urea production if desired.

The synthesis gas from the MEA stripping process still contains several hundred parts per million oxides of carbon. In order to use the gas in the ammonia converter the carbon oxides should be less than 10 ppm. Reducing the carbon oxides to the required level is best accomplished by methanation. This is done by heating the gas to about 300-400 °C and passing it over a nickel catalyst where the carbon oxides and hydrogen react to form methane and water:

$$CO + 3\ H_2 \rightarrow CH_4 + H_2O$$

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$$

The methane formed does not have to be separated from the synthesis gas since it has no affect on the catalyst. Except for the water the gas from the methanation process is sufficiently pure to enter the ammonia converter. The water is removed from the gas when it is compressed prior to entering the converter.

A number of processes have been developed for ammonia production based on the original Haber-Bosch process. These processes differ primarily in the design of the converter used and the reaction conditions (primarily temperature and pressure) in the converter. Figure 16 is a simplified flowsheet typical of the ammonia process as it is practiced in the United States. In this process, natural gas free of sulfur is compressed to about 30 atmospheres and then mixed with high pressure steam. The resultant mixture flows to the primary reformer where it is indirectly heated to 1200 °C in the presence of a nickel catalyst. The reaction

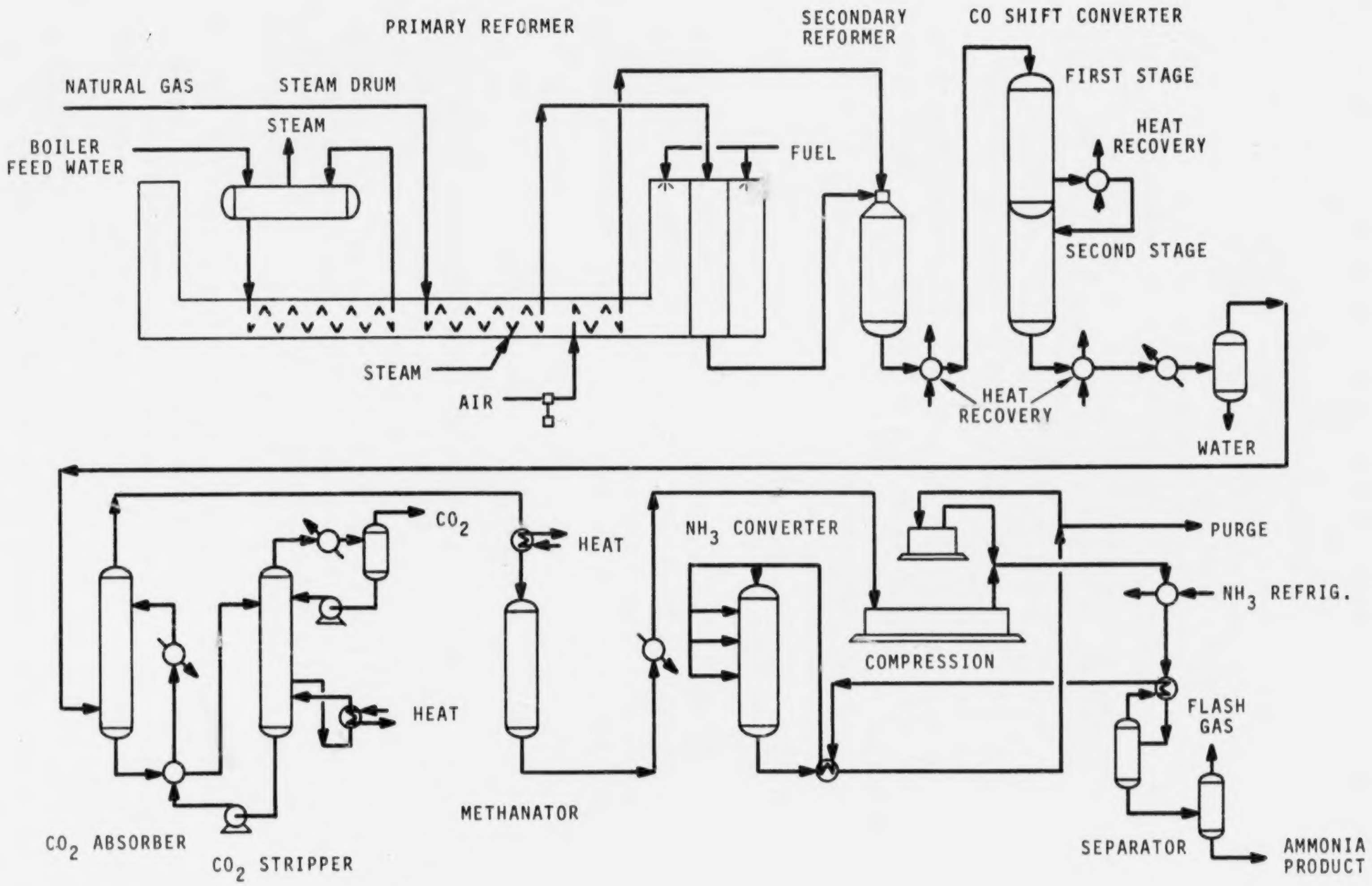

PRIMARY REFORMER
SECONDARY REFORMER
CO SHIFT CONVERTER
NATURAL GAS
STEAM DRUM
FIRST STAGE
BOILER FEED WATER
STEAM
FUEL
HEAT RECOVERY
SECOND STAGE
STEAM
AIR
HEAT RECOVERY
WATER
CO_2
HEAT
NH_3 CONVERTER
PURGE
NH_3 REFRIG.
COMPRESSION
HEAT
FLASH GAS
METHANATOR
CO_2 ABSORBER
CO_2 STRIPPER
SEPARATOR
AMMONIA PRODUCT

FIGURE 16 TYPICAL FLOWSHEET FOR AMMONIA PRODUCTION
(See pp 93-95 for Waste Stream Volume and Composition)

products flow to a secondary reformer where compressed air is added and a portion of the hydrocarbons and hydrogen burned. The heat released by the combustion of the gas raises the gas temperature and completes the conversion of the natural gas. The resultant gas mixture is cooled to about 400 °C and then mixed with high pressure steam. The steam-gas mixture is fed to the shift converter where the CO is converted to CO_2. The gas from the shift converter is cooled and scrubbed with a recirculating solution of MEA to remove the CO_2. The gas is then heated to 350 °C and fed to the methanator where any oxides of carbon are converted to methane. From the methanator the gas is cooled and sent to the compressors. The gas is compressed to the operating pressure of the ammonia converter. The compressed gas enters the synthesis converter loop where it mixes with the ammonia containing gas stream from the converter. The gas stream is cooled to condense the ammonia present and the ammonia product is removed in a liquid-gas separator. The remaining gas stream recycles to the converter. To prevent a buildup of inerts in the recirculating gas stream, a small portion of the gas is continually purged from the system. The ammonia synthesis reaction is exothermic and a considerable amount of heat must be removed from the converter loop by water cooling.

Ammonium Sulfate Production

Ammonium sulfate occupies a decreasing but still important position in the United States fertilizer industry. Almost all of the ammonium sulfate produced in the United States is prepared by reacting ammonia with sulfuric acid according to the reaction

$$2\ NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

Ammonium sulfate is normally produced as a crystalline product and control of the particle size is a major problem. In most instances the reaction between the acid and ammonia is carried out in the aqueous phase. The ammonium sulfate is precipitated by controlled evaporation and the product separated from the mother liquor by filtration or centrifugation. The separated product is then dried and screened.

The continuing importance of ammonium sulfate in the fertilizer industry is due primarily to the fact that at least one of the reactants can often be obtained from certain waste streams from other industries. Currently, about 60% of the ammonium sulfate production in the United States is by the recovery of ammonia, sulfuric acid or ammonium sulfate from industrial waste or by-product streams.(2)

The production of coke from coal by the steel industry results in the production of a coke oven gas which contains significant amounts of ammonia. By scrubbing the ammonia containing gas with sulfuric acid the steel industry produces large tonnages of ammonium sulfate.

In the petroleum and petrochemical industries significant quantities of waste sulfuric acid are generated. By reacting the spent acid waste with ammonia, fertilizer grade ammonium sulfate can be produced. The production of caprolactam results in the formation of large quantities of by-product ammonium sulfate (about four tons per tons of caprolactam). With the increasig production of caprolactam this is becoming a very important source of ammonium sulfate.(9)

The ammonium sulfate produced from industrial waste streams normally contains substantial amounts of impurities. These impurities do not usually interfere with the use of the ammonium sulfate as a fertilizer, although they may complicate the recovery of the solid product, by crystallization, from the aqueous phase.

Ammonium sulfate production from by-product and waste streams is often used as a means of pollution control. This being the case, there are no major water pollution problems which result directly from the by-product production of ammonium sulfate.

Substantial amounts of ammonium sulfate are produced from manufactured ammonia and sulfuric acid (approximately 40% of U.S. production), as opposed to recovery from waste streams. This manufacture of ammonium sulfate can lead to significant water pollution problems.

The major problem in reacting ammonia and acid to produce ammonium sulfate is controlling the particle size of the sulfate in the reaction system. A variety of reaction systems have been developed to produce a suitable product. Regardless of the reaction system used the basic operations required for ammonium sulfate production are the same. They consist of reacting the ammonia and acid in an aqueous system, evaporating water to precipitate the ammonium sulfate, separating the sulfate crystals from the aqueous phase, drying the solids, and then screening to obtain the desired size fraction. A flowsheet typical of ammonium sulfate production using synthetic ammonia is shown in Figure 17.

In this process, anhydrous ammonia is fed to a crystallizer where it is mixed with sulfuric acid and a slurry of ammonium

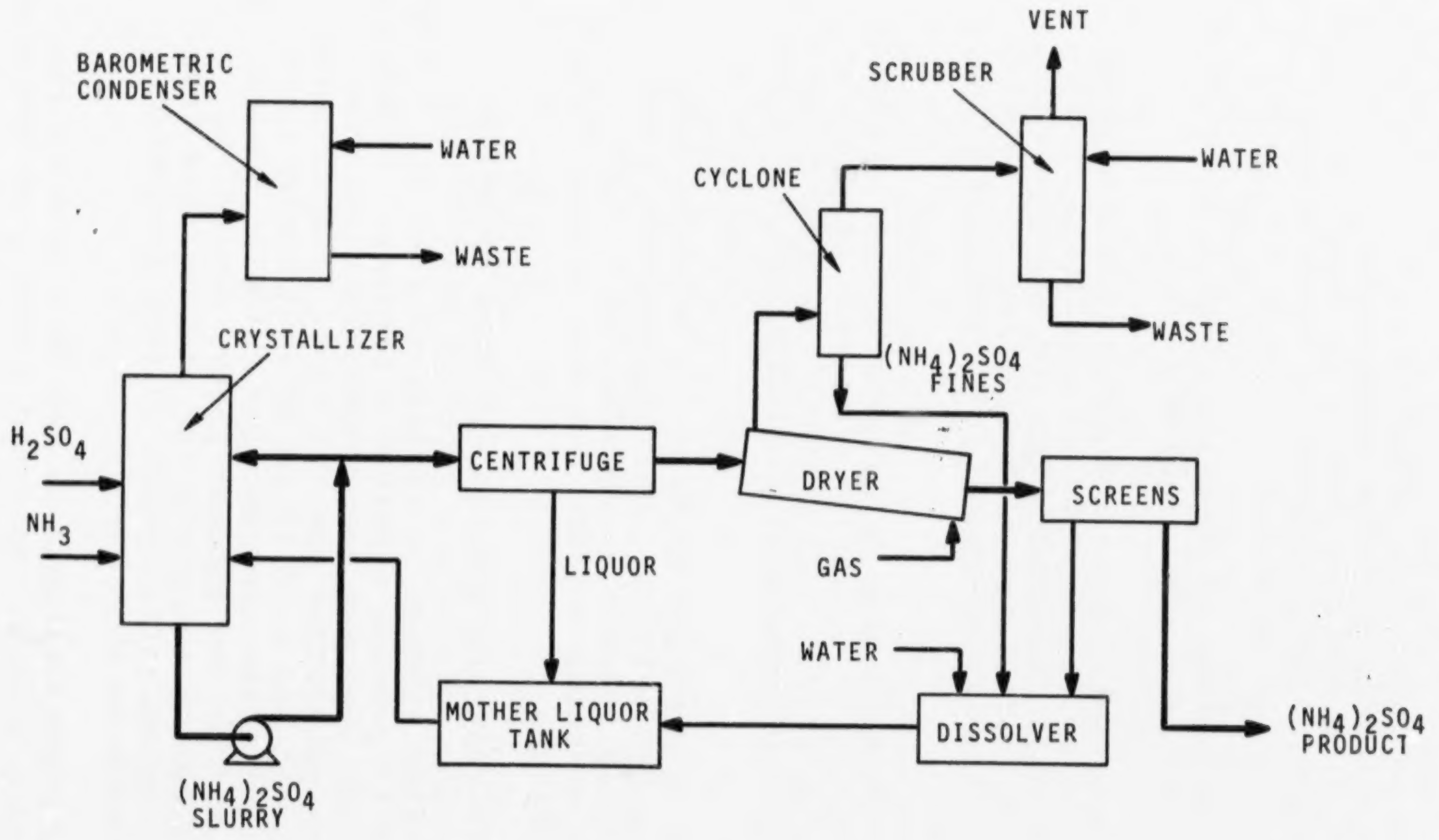

BAROMETRIC CONDENSER
WATER
WASTE
CRYSTALLIZER
H_2SO_4
NH_3
CENTRIFUGE
LIQUOR
MOTHER LIQUOR TANK
$(NH_4)_2SO_4$ SLURRY
CYCLONE
$(NH_4)_2SO_4$ FINES
DRYER
GAS
SCRUBBER
VENT
WATER
WASTE
SCREENS
WATER
DISSOLVER
$(NH_4)_2SO_4$ PRODUCT

FIGURE 17 TYPICAL FLOWSHEET FOR AMMONIUM SULFATE PRODUCTION USING SYNTHETIC AMMONIA
(See p 100 for Waste Stream Volume and Composition)

sulfate crystals. Circulation of the slurry in the crystallizer is designed to give a product of the desired particle size. The reaction of sulfuric acid and ammonia is exothermic and the heat liberated results in the evaporation of water and precipitation of the ammonium sulfate.

A continuous stream of slurry is removed from the crystallizer and sent to a continuous centrifuge where the liquor is removed. The crystal cake discharges from the centrifuge to a gas fired dryer. In the dryer the ammonium sulfate particles are dried to less than 0.1% moisture. The dried product is cooled and screened to the desired particle size.

The saturated liquor from the centrifuge flows to a mother liquor holding tank and then recycles to the reactor. The ammonium sulfate oversize and undersize from the screens flow to a tank where they are dissolved. The resulting solution then returns to the mother liquor holding tank.

The offgas from the reactor consists primarily of water vapor but does contain small amounts of ammonia and sulfate. This stream is condensed in a barometric condenser and discharged. The gas stream from the product dryer contains ammonium sulfate particulate matter and small amounts of ammonia. The gas passes through cyclones to remove the solids and is then scrubbed with water to remove the ammonia. The fines collected in the cyclone are sent to the dissolving tank where they are dissolved with the rejects from the screens. The scrubber solution discharges to the aqueous disposal system.

Ammonium sulfate crystals can present handling problems due to caking. Careful drying can help to reduce caking; but in some plants the practice is to coat the ammonium sulfate particles with an inert material such as clay to prevent caking.

Ammonium Nitrate Production

Ammonium nitrate is a major source of fertilizer nitrogen in the United States. It makes an excellent fertilizer material because of its high nitrogen content (35%) and low cost of preparation. Large amounts of ammonium nitrate are used in direct fertilizer applications. In addition, it is widely used in mixed fertilizers, both liquid and solid, and in nitrogen solutions.

Almost all ammonium nitrate production in the United States is based on the reaction of ammonia with nitric acid:

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

The acid-ammonia neutralization reaction is straightforward and easily carried out. The major problems in ammonium nitrate production relate to recovery of the solid product from the neutralized solution. The hazardous nature of solid ammonium nitrate adds to the recovery problems. There are three major processes for preparing solid ammonium nitrate: crystallization, flaking, and prilling.(19) Of the three, prilling is the most important in the United States.

The basic steps in the production of solid ammonium nitrate are reaction of the acid and ammonia, concentration of the resultant solution, and conversion to solid ammonia nitrate. Figure 18 is a simplified flowsheet typical of the ammonium nitrate process and showing the major alternatives for the recovery of the solid ammonium nitrate. Typically, anhydrous ammonia and nitric acid are reacted in a neutralizer (the reaction can be carried out under vacuum, at atmospheric pressure, or at an elevated pressure). The reaction is highly exothermic and water evaporates from the reaction mixture to give a concentrated solution containing 80-85% ammonium nitrate. The solution from the neutralizer flows to a concentrator where additional water is evaporated to raise the ammonium nitrate concentration to about 95%.

If a prilled product is desired, the solution from the concentrator is pumped to the top of a tall tower and sprayed down into a rising current of heated air. As the droplets of solution descend in the tower water is evaporated and spherical particles of solid ammonium nitrate are formed. The size of the particles produced is controlled by spray nozzles, and is usually in the range of 8-16 mesh.(9) The particles from the prilling tower are further dried in a gas fired dryer to reduce the moisture of the ammonium nitrate to less than 0.5%. The dried product, after cooling, is screened and then coated with an anti-caking agent such as clay. The undersize particles from the screens are dissolved and recycled to the concentrator.

When crystalline ammonium nitrate is desired, the solution from the concentrator is fed to a continuous crystallizer similar to that used for ammonium sulfate production. In the crystallizer the solution is cooled by vacuum evaporation to produce the crystalline ammonium nitrate. The crystalline product obtained is withdrawn from the crystallizer and sent to a continuous centrifuge where the crystals and liquor are separated. The liquor from the centrifuge recycles to the crystallizer. The ammonium nitrate crystals are dried to less than 0.1% water, cooled, screened, and coated with an anti-caking agent. The undersize particles from the screens are recycled to the crystallizer.

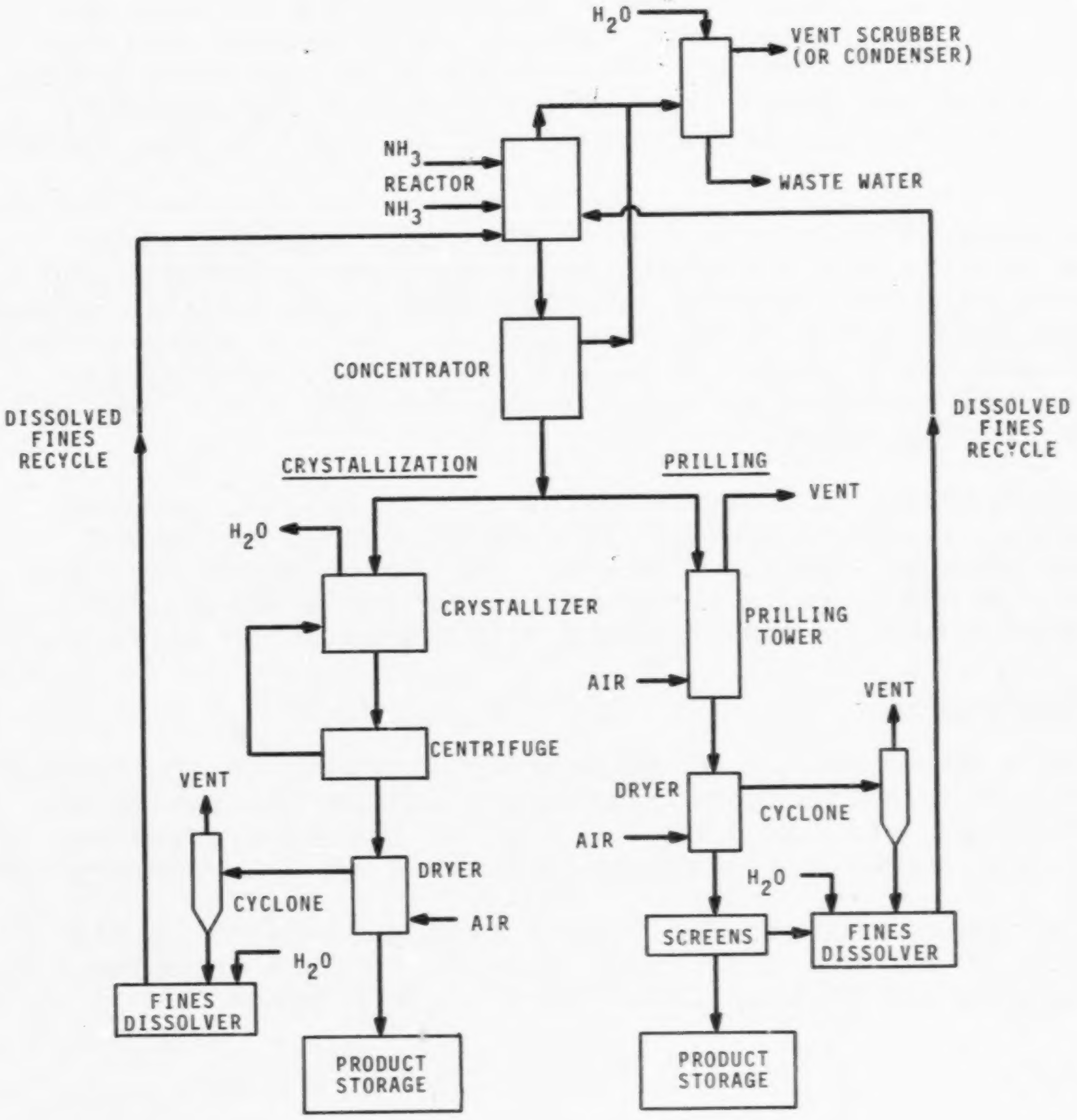

H2O
VENT SCRUBBER (OR CONDENSER)
NH3
REACTOR
NH3
WASTE WATER
CONCENTRATOR
DISSOLVED FINES RECYCLE
DISSOLVED FINES RECYCLE
CRYSTALLIZATION
PRILLING
VENT
H2O
CRYSTALLIZER
PRILLING TOWER
AIR
VENT
CENTRIFUGE
VENT
DRYER
CYCLONE
AIR
DRYER
CYCLONE
AIR
H2O
H2O
SCREENS
FINES DISSOLVER
FINES DISSOLVER
PRODUCT STORAGE
PRODUCT STORAGE

FIGURE 18 FLOWSHEET FOR AMMONIUM NITRATE PRODUCTION
(See p 100 for Waste Stream Volume and Composition)

In the ammonium nitrate processes as described, there are several operations which generate waste streams that can present disposal problems. In the neutralizer, a small amount of ammonia (and nitric acid) can be lost with the water evaporated. Condensation of the water vapor results in a waste stream contaminated with ammonia and nitrate ion. Operation of the concentrator can produce a similar waste stream. In the prilling process, the air stream which leaves the top of the prilling tower contains a mixture of water vapor, ammonia, and nitrogen oxides. When this gas stream is scrubbed with water a waste stream containing ammonia is generated. The offgas from the dryer contains ammonium nitrate particles. The solids are separated by means of a cyclone, redissolved, and recycled to the concentrator.

In the crystallization process, the water evaporated in the crystallizer can contain small amounts of ammonia and nitric acid. Condensation of the water gives a waste stream contaminated with both ammonia and nitrate. The dryer used in the crystallization processes present the same types of disposal problems as are encountered with the dryer in the prilling process.

When an ammonium nitrate solution is the desired product the neutralization reaction is carried out in equipment similar to that described above. The major waste disposal problem is the aqueous waste stream from the neutralizer condenser which is contaminated with ammonia and nitrate.

Urea Production

Urea is a major source of fertilizer nitrogen in the United States. Its use in fertilizer applications is growing at a rapid rate, and based on the tons of nitrogen supplied trails only ammonia and ammonium nitrate in U.S. consumption.

All urea production in the United States is based on the reaction of ammonia and carbon dioxide to form ammonium carbamate which is then dehydrated to form urea:

$$CO_2 + 2\,NH_3 \rightarrow NH_4CO_2NH_2$$

$$NH_4CO_2NH_2 \rightarrow NH_2CONH_2 + H_2O$$

Since the raw materials for urea production are ammonia and carbon dioxide, urea plants are almost always operated in conjunction with an ammonia plant. The ammonia plant serves not only as the source of anhydrous ammonia, but also as the source of high purity carbon dioxide which is a by-product from the preparation of the ammonia synthesis gas.

The reaction between ammonia and carbon dioxide is carried out in a pressurized reactor to form a solution containing urea, ammonium carbamate and water. The ammonia-carbon dioxide reaction is strongly exothermic and under the conditions found in the urea reactor proceeds almost to completion. The dehydration reaction is endothermic and under the reaction conditions proceeds to 40-60% completion. Overall, the two reactions are exothermic and external cooling must be provided to maintain the reaction conditions. Both reactions are reversible and the equilibria obtained will depend on the pressure, temperature, and concentrations of the reactants and products. Urea formation increases with increasing temperature. Increasing the temperature, however, requires an increase in operating pressure because the urea only forms in the liquid phase. Since the pressure required to maintain the liquid phase increases very rapidly with temperature the reactor is normally held below 210 °C. Depending on the process being used, the reactor temperatures vary from 170-210 °C and the pressure from 135-400 atmospheres.

The product stream from the reactor is a mixture of urea, ammonium carbamate, water, unreacted ammonia, and carbon dioxide. An excess of ammonia is always used so the CO_2 concentration in the exit stream is low. The final steps in the urea process involve the decomposition of the ammonium carbamate, recovery of the urea product in usable form, and possible recycle of the unreacted ammonia and carbon dioxide.

Basically, there are three types of processes for urea production which differ primarily in the way in which the unconverted ammonia and carbon dioxide from the reactor are handled:

1. Once-through process - In the once-through process no attempt is made to recycle the unreacted ammonia and carbon dioxide. Instead, the offgas ammonia is used in the production of other fertilizer products or intermediates (i.e., HNO_3, NH_4NO_3, etc.).
2. Partial Recycle Process. In the partial recycle process a portion of the unreacted ammonia is recovered and recycled while the carbon dioxide is used in other processes or is wasted.
3. Total Recycle Process. In the total recycle process both the unreacted ammonia and carbon dioxide are recovered and recycled to the urea reactor.

The choice of which process to use depends on a number of factors, and requires a detailed analysis to arrive at a satisfactory decision. The once-through process has the advantage of a relatively low capital cost. However, its economic operation requires that the unreacted ammonia can be used in other processes and that carbon dioxide be available at low cost. Partial Recycle and Total Recycle are less dependent on raw material costs and on integrating with other processes, but they have significantly higher capital costs. The current study indicates that greater than 50% of the urea plants in the United States use total recycle.

After the ammonium carbamate, ammonia, and carbon dioxide are removed, the product solution contains about 75-80% urea. Subsequent processing of the urea solution depends on the product form required. If the urea is used in liquid fertilizers or nitrogen solutions, no further processing is required except for the final blending operation. If a solid product is desired, there are three major methods for converting the urea solution to a solid: (1) crystallization of the urea, (2) prilling, and (3) crystallization followed by prilling.

The selection of the method of solidification depends primarily on the end use for the urea and on the biuret content that can be tolerated in the product. When urea is heated it decomposes to form biuret according to the reaction

$$2\ NH_2CONH_2 \rightleftarrows NH_2CONHCONH_2 + NH_3$$

The decomposition reaction proceeds relatively slowly below 120 °C, but becomes quite rapid as the temperature approaches the melting point of urea (132.7 °C). In making prilled urea it is necessary to melt the urea. This can result in a significant biuret content in the final product (greater than 1%). Biuret formation is much less in making crystalline urea and by careful control can be held below 0.1%. By using crystallization followed by prilling, it is possible to obtain a prilled product containing less than 0.5% biuret. In many fertilizer applications the biuret concentration of the urea must be kept as low as possible because of possible crop damage. This means that product end use has a significant effect on selection of the solidification process used. Fertilizer grade urea normally contains less than 1% biuret, but can contain up to 2.5%. Technical grade urea for industrial purposes may contain as little as 0.1% biuret.

Urea has a tendency to cake unless the moisture content is kept low. Both crystalline and prilled urea are dried to a moisture content of less than 0.3% moisture, and should be stored in moisture-proof bags to prevent adsorption of water. Urea frequently is conditioned with clay or similar materials to prevent caking.

A number of companies have developed urea processes and almost every process has the option of once-through, partial recycle, or total recycle operation. The differences between the various processes are involved primarily with the ways of handling the ammonia and carbon dioxide offgases from the ammonium carbamate decomposition. Regardless of the process design used, the basic operation of urea production are the same and the waste streams generated are similar.

Figure 19 presents a simplified flowsheet typical of urea production using total recycle and a prilling tower. Anhydrous liquid ammonia is fed to a reactor where it is reacted with carbon dioxide to give a solution of urea, ammonium carbamate, and water. The temperature in the reactor is about 185 °C and the pressure 200 atmospheres. The reaction mixture flows to a stripping section where its pressure is reduced to about 20 atmospheres. The excess ammonia is released from solution and part of the carbamate is dehydrated. The gases from the stripper are washed to give a pure ammonia gas stream and an ammonium carbamate solution. The ammonia is recycled to the ammonia feed systems and the carbamate solution is recycled to the reactor. The solution from the stripper flows to a decomposer (operating at about 5 atmospheres pressure) where the rest of the carbamate dehydrates. The resultant solution, which contains 75-80% urea, flows to a concentrator. The vent gases from the decomposer are condensed to form a dilute ammonium carbamate solution which recycles to wash the gas stream from the stripper.

In the concentrator, water is evaporated to raise the urea concentration to greater than 98%. The molten urea from the concentrator is pumped to the top of a prilling tower where it is sprayed downward against a stream of cold air. The urea prills from the tower are cooled, screened and packaged for storage.

The water evaporated from the concentrator contains small amounts of ammonia. The water is condensed and the ammonia is stripped from the condensate with steam. The water is discharged to the environment and the ammonia steam gas stream is recycled to the process.

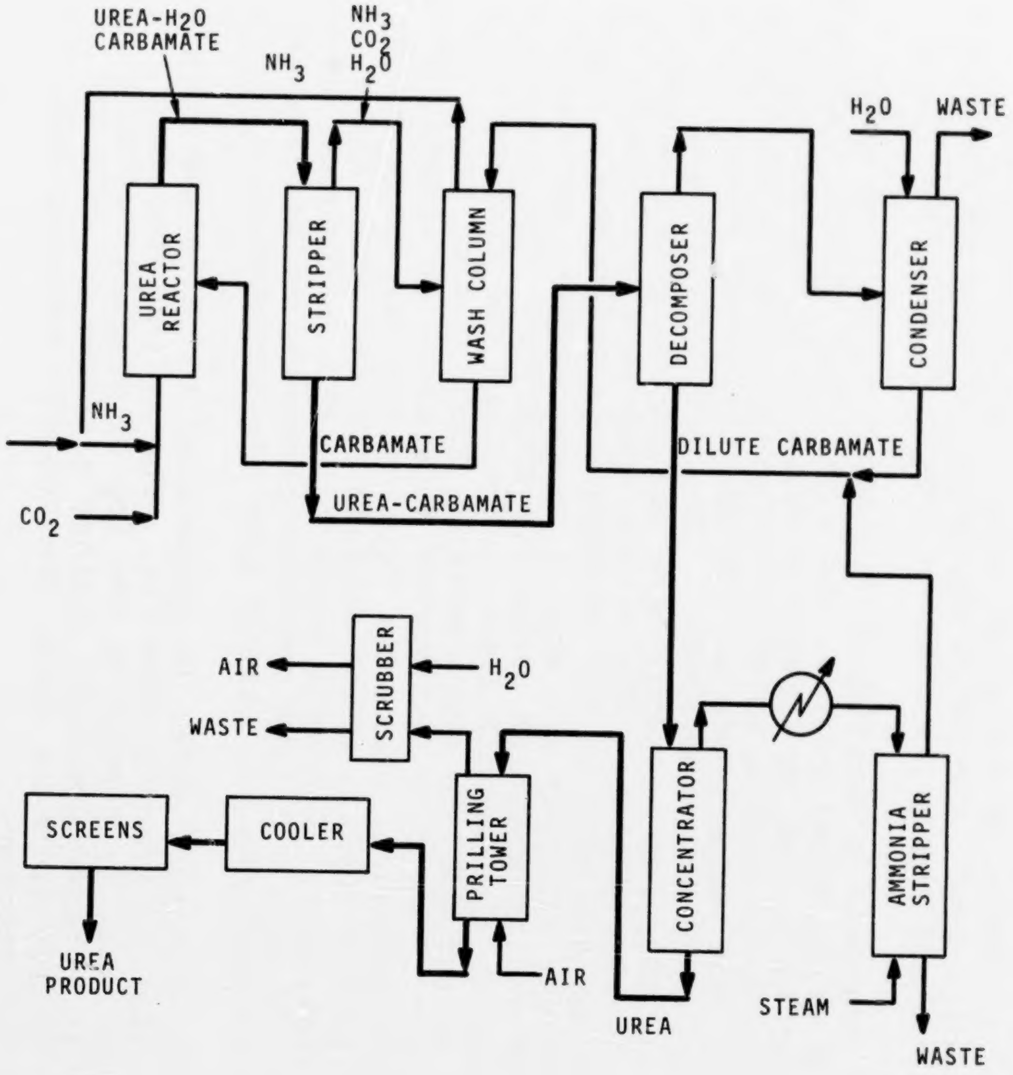

UREA-H2O CARBAMATE
NH3
NH3 CO2 H2O
H2O
WASTE
UREA REACTOR
STRIPPER
WASH COLUMN
DECOMPOSER
CONDENSER
NH3
CARBAMATE
DILUTE CARBAMATE
CO2
UREA-CARBAMATE
AIR
H2O
SCRUBBER
WASTE
SCREENS
COOLER
PRILLING TOWER
CONCENTRATOR
AMMONIA STRIPPER
UREA PRODUCT
AIR
UREA
STEAM
WASTE

FIGURE 19 TYPICAL FLOWSHEET FOR UREA PRODUCTION - TOTAL RECYCLE AND PRILLING TOWER
(See pp 97-99 for Waste Stream Volume and Composition)

The air stream from the prilling tower also contains some ammonia. Air pollution requirements may necessitate water scrubbing the ammonia from the air prior to discharge. The scrubber solution may then be treated to remove the ammonia before the water is discharged.

PHOSPHATE FERTILIZER PRODUCTION PROCESSES

Wet Process Phosphoric Acid Production

In the wet process for preparing phosphoric acid the phosphate rock (principally fluorapatite) is reacted with a strong mineral acid to convert the tricalcium phosphate to orthophosphoric acid (H_3PO_4). Hydrochloric and nitric acids can be used, but the preferred route is the reaction with sulfuric aicd. The overall reaction of the tricalcium phosphate and sulfuric acid results in the formation of phosphoric acid and calcium sulfate:

$$Ca_3(PO_4)_2 + 3\ H_2SO_4 \rightarrow 3\ CaSO_4\downarrow + 2\ H_3PO_4$$

The reaction proceeds in several steps but the overall reaction is as written above.

The calcium sulfate formed is relatively insoluble in phosphoric acid and it precipitates from solution. Depending on reaction conditions, the calcium sulfate can crystallize out as an anhydrite ($CaSO_4$), a hemihydrate ($CaSO_4 \cdot 1/2H_2O$), or a dihydrate ($CaSO_4 \cdot 2H_2O$) commonly referred to as gypsum.

Almost all phosphate rock from a given deposit will contain fluorine and P_2O_5 in a relatively constant ratio which approximates that for fluorapatite. The fluoride content of the rock is attacked by the sulfuric acid during acidulation with the formation of calcium sulfate and hydrogen fluoride:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4\downarrow + 2\ HF_{(aq)}$$

The overall reaction of fluorapatite with sulfuric acid is, therefore,

$$3Ca_3(PO_4)_2 \cdot CaF_{2\,(s)} + 10\ H_2SO_{4\,(aq)} + 10\ X\ H_2O_{(1)}$$
$$\rightarrow 6\ H_3PO_{4\,(aq)} + 2\ HF_{(aq)} + 10\ CaSO_4 \cdot XH_2O_{(s)}$$

where X can be zero, 1/2 or 2 depending on the reaction conditions.

The hydrogen fluoride which forms will react with any silica or silicates in the rock to form silicon tetrafluoride which then hydrolyzes to form fluosilicic acid:

$$SiO_2 + 4\ HF_{(aq)} \rightarrow SiF_4 + 2\ H_2O$$

$$3\ SiF_4 + 2\ H_2O \rightarrow 2\ H_2SiF_6 + SiO_2\downarrow .$$

Depending on reaction conditions, some of the fluosilicic acid will decompose with the volatilization of silicon tetrafluoride, according to

$$H_2SiF_6 \rightarrow SiF_4\uparrow + 2\ HF_{(aq)}.$$

Depending on the impurities in the rock, there are a number of minor reactions which can occur during acidulation. If any carbonate is present, it will react with the sulfuric acid with the evolution of carbon dioxide:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4\downarrow + CO_2 + H_2O .$$

If any sodium and potassium are present alkali fluosilicates will be formed:

$$Na_2O + H_2SiF_6 \rightarrow Na_2SiF_6 + H_2O .$$

These compounds can be particularly troublesome. They are a principal cause of scaling in equipment and piping, and are corrosive.

If hydrochloric acid or nitric acid is used to attack the rock, the calcium by-product is soluble in the phosphoric acid. The reactions are:

$$Ca_3(PO_4)_2 + 6\ HCl \rightarrow 3\ CaCl_2 + 2\ H_3PO_4$$

$$Ca_3(PO_4)_2 + 6\ HNO_3 \rightarrow 3\ Ca(NO_3)_2 + 2\ H_3PO_4 .$$

The preparation of phosphoric acid by either reaction requires a method for removing the soluble calcium salt from the acid. Phosphoric acid processes have been developed which utilize either hydrochloric or nitric acid but none are used commercially in the United States.

The production of phosphoric acid by the wet process using sulfuric acid is the principal source of fertilizer phosphoric acid in the United States. Preparation of H_3PO_4 by the wet process is strongly influenced by the nature of the calcium sulfate by-product. The P_2O_5 recovery from the phosphate rock, the filtration rate of the calcium sulfate-phosphoric acid slurry, and the strength of H_3PO_4 produced are all related to the form of the calcium sulfate produced. It is possible to precipitate the calcium sulfate in three different forms and this has led to the development of three general types of wet processes.

1. The anhydrite process
2. The hemihydrate process
3. The dihydrate process

Various modifications of the three types of processes exist and Slack(9) has further subdivided the various processes into the following classifications:

1. Continuous pure dihydrate crystallization (standard U.S. process)
2. Continuous primary dihydrate crystallization with subsequent recrystallization into hemihydrate
3. Continuous pure hemihydrate crystallization
4. Continuous crystallization of inactivated hemihydrate with partial simultaneous crystallization of dihydrate
5. Continuous primary hemihydrate crystallization and subsequent recrystallization to dihydrate before filtration
6. Continuous hemihydrate crystallization in strong acid, acid separation and dilution and recrystallization to dihydrate
7. Continuous primary hemihydrate crystallization and secondary anhydrite recrystallization
8. Continuous pure anhydrite crystallization
9. Anhydrite crystallization with batchwise reactor charging
10. Production of anhydrite clinker followed by leaching.

In the United States only the dihydrate process has achieved any commercial significance, and a number of companies have developed processes based on the precipitation of the dihydrate. The processes vary principally in the design of the reactor systems in which the rock and sulfuric acid are reacted and in the method used to filter the gypsum from the product acid. There are also variations in the types of evaporators which are used to concentrate the phosphoric acid from the filters.

Regardless of the type of dihydrate process design used, the basic operations are the same. A flowsheet typical of the dihydrate processes and showing the basic operations is shown in Figure 20. Typically, beneficiated phosphate rock, containing 30-35% P_2O_5, is ground to 60% -200 mesh. The ground rock is fed continuously to a reaction system where it is mixed with sulfuric acid and a recycle stream of dilute phosphoric acid. The reaction system consists of one or more digestion tanks depending on the design. The more recent developments favor the use of a single, large compartmented tank. In the digestion tank(s) the rock and acid react to form gypsum (dihydrate) and phosphoric acid. To obtain complete reaction of the rock, the rock-gypsum-acid slurry is rapidly circulated between the digestion tanks or the compartments of a single tank.

To insure the formation of dihydrate, the temperature in the digestor is maintained at about 75 °C. Since the reaction between the phosphate rock and sulfuric acid is exothermic, heat must be removed from the digestor system to maintain temperature control. The amount of heat to be removed depends largely on the concentration of the sulfuric acid. In most plants the concentration of the sulfuric acid used will be between 77 and 98% with 93% acid being the norm. The heat can be removed from the system by a number of ways including vacuum coolers, air sparging, and dilution and cooling of the sulfuric acid prior to use.

Retention time in the digestor is in the range of 3-8 hours. The extraction of P_2O_5 from the rock normally exceeds 96% and the strength of phosphoric acid produced is in the range of 30-32% P_2O_5. The gypsum formed must be easily filtered and retain a minimum of P_2O_5.

The acid slurry flows from the digestor to a filter system where the gypsum is removed. Good filter design is quite complex, and a number of companies have developed filters especially for the phosphoric acid industry. Typically the filter system yields two phosphoric acid streams: a 30-32% P_2O_5 product stream and a stream containing about 20% P_2O_5 which recycles to the digestor. The gypsum cake is thoroughly washed with water to remove residual acid. The gypsum cake from the filter is slurried with water and discharged to waste.

The 30-32% P_2O_5 product stream from the filter is sent to an evaporator system where it is concentrated to give a phosphoric acid product containing about 54% P_2O_5. Because of impurity precipitation and scaling, concentrator design is quite complex and a number of companies have developed a variety of concentrators designed to control scaling.

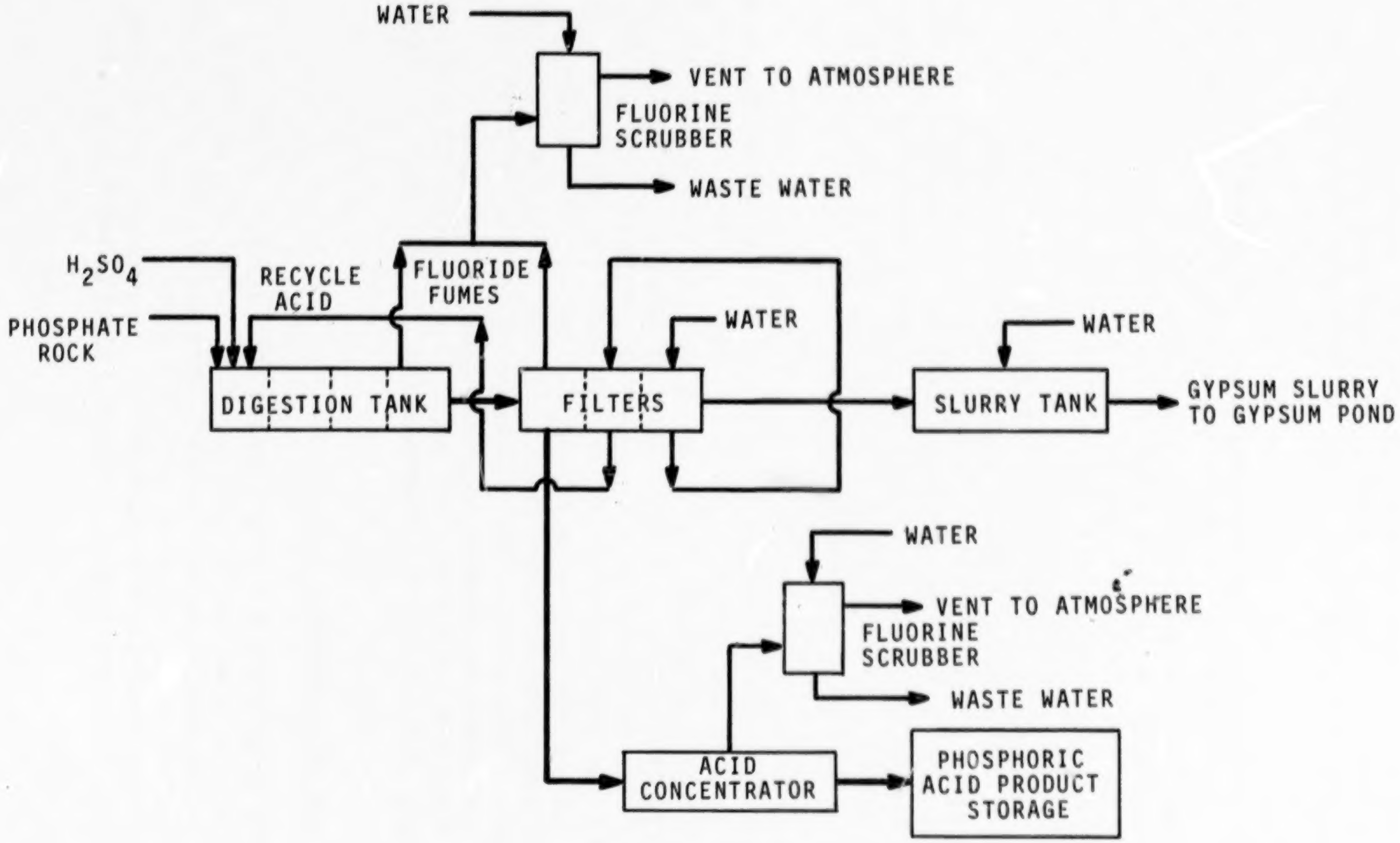

WATER
VENT TO ATMOSPHERE
FLUORINE SCRUBBER
WASTE WATER
H_2SO_4
PHOSPHATE ROCK
RECYCLE ACID
FLUORIDE FUMES
DIGESTION TANK
FILTERS
WATER
SLURRY TANK
WATER
GYPSUM SLURRY TO GYPSUM POND
WATER
VENT TO ATMOSPHERE
FLUORINE SCRUBBER
WASTE WATER
ACID CONCENTRATOR
PHOSPHORIC ACID PRODUCT STORAGE

FIGURE 20 WET PROCESS PHOSPHORIC ACID FLOWSHEET
(See pp 103-107 for Waste Stream Volume and Composition)

If the product acid is to be used fairly soon for fertilizer production, no attempt is made to remove the impurities which precipitate. If the acid is to be stored or shipped before use, the solids are normally removed. This can be done by storing the acid for several days in tanks and allowing the solids to settle. The thickened solids, containing a substantial amount of P_2O_5, are collected and normally used in fertilizer manufacture. The clarified acid is ready for shipment.

As mentioned previously, any fluorine in the phosphate rock will react in the digestor to form HF and H_2SiF_6. Fluorine will be released to the atmosphere as SiF_4, HF, and fluoride dust in varying amounts in the vent gases from the phosphoric acid process. To control air pollution it is necessary that the fluorine evolved be removed from the gas streams prior to discharge to the atmosphere. The major source of fluorine evolution are the reactor, the concentrator, and the filter. It is standard practice to water-scrub the vent gases for fluoride removal. This results in a waste water stream that must be treated for fluoride removal before discharge to the environment. It is normal practice in some plants to recover part of the fluoride values from the waste water as fluosilicates and the resultant contaminated water is sent to the gypsum pond.

The wet process phosphoric acid plant produces large tonnages of gypsum (on the order of 4.5 tons of gypsum per ton of P_2O_5 product). It is general practice to store this gypsum in diked areas called gypsum ponds. The slurried gypsum from the filter is pumped to these ponds where the gypsum settles out. The clarified water is recycled back to the various parts of the process. The water in the gypsum pond slowly increases in phosphate and fluoride content until an equilibrium concentration is reached. The pH of the water decreases to between 1 and 2. If it becomes necessary to discharge the gypsum pond water to the environment, it must be treated to reduce the fluorine and phosphate to acceptable levels and to control the pH.

Electric Furnace Phosphoric Acid

Phosphoric acid produced by the electric furnace process is of higher purity than acid produced by the wet process. Furnace grade phosphoric acid is used primarily in the chemical and food industries and, at the present time, finds only limited use in the fertilizer industry. However, with the increased use of high analysis liquid fertilizers and the potential loss of the detergent market, it is quite possible that furnace grade phosphoric acid will find substantially increased use in the fertilizer industry in the future.

While there are a number of companies which produce furnace grade phosphoric acid, the processes used by the various producers are quite similar. One does not find the differences in equipment and operation in the furnace process that occur in the wet processes.

Basically, the furnace processes involve the reaction of phosphate rock with carbon and silica in an electric furnace to form elemental phosphorus. The overall reaction can be written as follows:

$$2\ Ca_3(PO_4)_2 + 6\ SiO_2 + 10\ C \rightarrow 6\ CaSiO_3 + P_4\uparrow + 10\ CO\uparrow$$

The elemental phosphorus which volatilizes from the furnace is collected and oxidized to P_2O_5. The P_2O_5 is absorbed in water to give a concentrated orthophosphoric acid:

$$P_4 + 5O_2 \rightarrow 2\ P_2O_5$$

$$P_2O_5 + 3\ H_2O \rightarrow 2\ H_3PO_4$$

Two side reactions of importance occur in the furnace. Any iron oxide in the rock, silica or carbon is reduced to elemental iron:

$$Fe_2O_3 + 3\ C \rightarrow 2\ Fe + 3\ CO$$

The elemental iron then reacts with phosphorus to form ferrophosphorus,

$$8\ Fe + P_4 \rightarrow 4\ Fe_2P$$

The ferrophosphorus is stable under the furnace reaction conditions and represents a direct loss of phosphorus. In standard furnace operation the ferrophosphorus and calcium silicate slag are allowed to build up in the furnace to predetermined levels and are then tapped from the furnace in separate liquid phases.

About 10-20% of the fluorine in the rock in the furnace is converted to volatile silicon tetrafluoride and leaves with the phosphorus. The rest of the fluorine stays with the calcium silicate slag (probably as CaF_2).

The furnace process can use phosphate rock of any grade, but since silica is required as a raw material in the process a low phosphate, high-silica rock is preferred. Phosphate rock from the Tennessee area and from the Western United States is particularly suitable for the furnace process.

A flowsheet typical of the furnace process is shown in Figure 21. Typically, ground phosphate rock is agglomerated to give about 8 mesh particles. A variety of methods such as pelletizing, briquetting, or nodulizing can be used to agglomerate the rock. The rock is then blended with a controlled amount of low ash coke and silica which is low in iron and lime. The resultant mixture is charged to the electric furnace which is equipped with carbon electrodes. In the furnace the components of the charge react at about 1400 °C to form elemental phosphorus, calcium silicate slag, and ferrophosphorus. The ferrophosphorus forms a molten layer in the furnace with the slag layer on top of the ferrophosphorus layer. The slag layer is tapped from the furnace about once an hour, and the ferrophosphorus layer is tapped twice a day.

The phosphorus leaves the furnace, through openings in the furnace cover, with the CO and fine particulate matter. The dust is removed from the gas stream by heated (300 °C) electrostatic precipitators. The cleaned gases flow to a condensing unit where the phosphorus is condensed with water. The molten phosphorus is collected under water and pumped to tanks where it is stored under water.

The molten phosphorus flows from the storage tank to a combustion chamber where it is burned at 1500-1700 °C in air to form P_2O_5. The hot P_2O_5 vapor passes through a gas cooler to a hydration tower where the P_2O_5 is reacted with water to form H_3PO_4. The product acid normally contains 54% P_2O_5 but higher concentrations can be produced.

The offgas from the hydration tower contains some P_2O_5 and phosphoric acid mist. This gas stream is treated by precipitators or scrubbers to react the P_2O_5 and recover the acid prior to discharge to the atmosphere. The acid recovered is combined with the product from the hydrator.

When the slag is tapped from the furnace some P_2O_5 and fluorine (as SiF_4) are evolved from the slag while it is cooling. Air pollution regulations usually require that these evolutions be controlled, so the gases are normally scrubbed with water to remove the fluoride and P_2O_5.

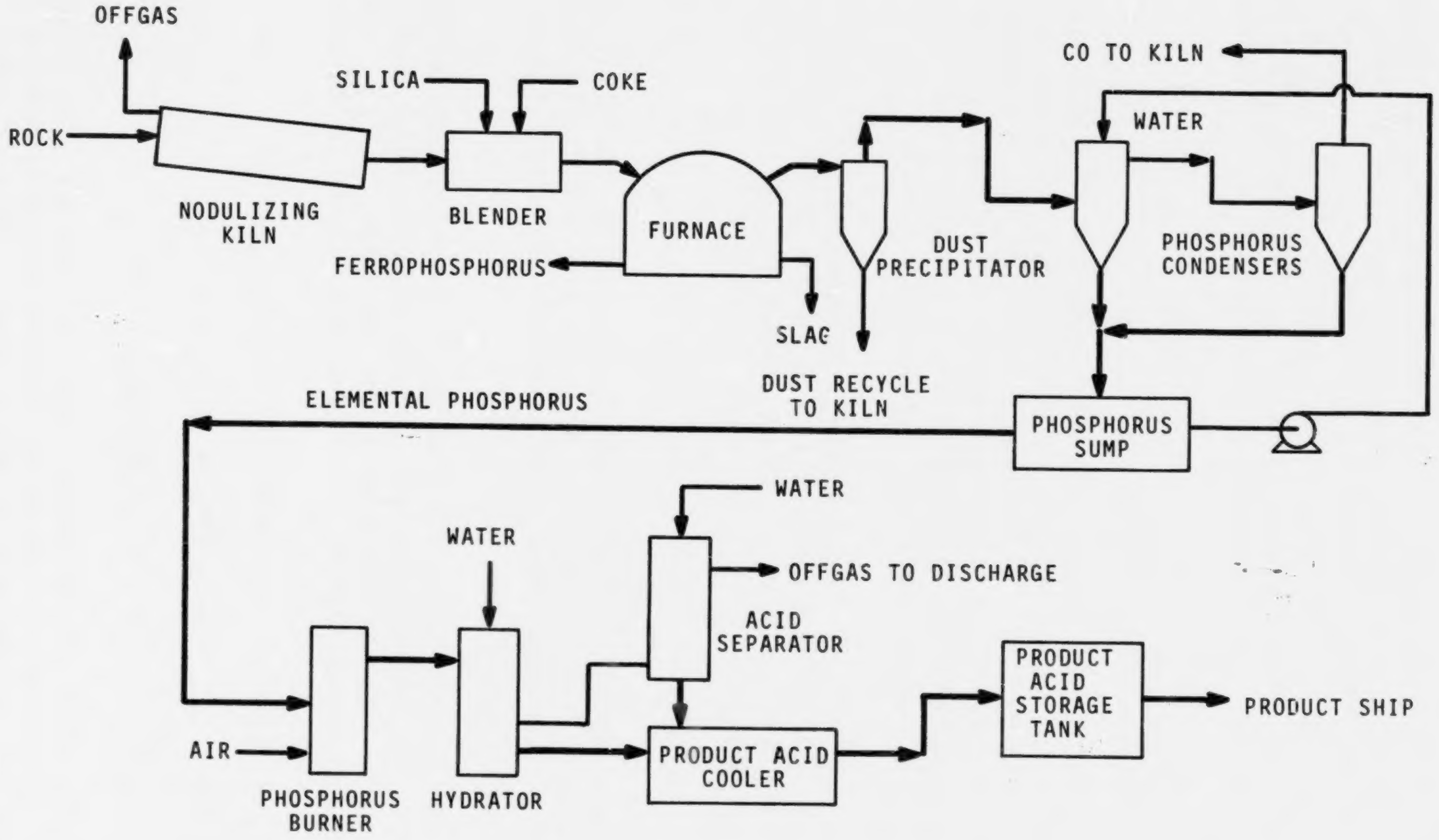

OFFGAS
ROCK
SILICA
COKE
NODULIZING KILN
BLENDER
FURNACE
FERROPHOSPHORUS
SLAG
DUST PRECIPITATOR
DUST RECYCLE TO KILN
CO TO KILN
WATER
PHOSPHORUS CONDENSERS
PHOSPHORUS SUMP
ELEMENTAL PHOSPHORUS
WATER
WATER
OFFGAS TO DISCHARGE
ACID SEPARATOR
AIR
PHOSPHORUS BURNER
HYDRATOR
PRODUCT ACID COOLER
PRODUCT ACID STORAGE TANK
PRODUCT SHIP

FIGURE 21 FLOWSHEET FOR PHOSPHORIC ACID PRODUCTION BY THE ELECTRIC FURNACE PROCESS (See pp 107-108 for Waste Stream Volume and Composition)

A portion of the fluoride in the phosphate rock leaves the furnace with the CO-phosphorus offgas. A portion of this fluoride, as particulate matter, is collected in the precipitator, while the volatile fluoride is collected with the phosphorus in the water-sprayed condenser.

Condensation of the phosphorus with water and its subsequent storage and handling under water leads to the formation of (1) a waste water stream that is contaminated with phosphorus and fluoride (so called phossy water), and (2) a phosphorus sludge emulsion comprised of water, phosphorus particles, and solids. Both waste streams present disposal problems.

Normal Superphosphate Production

Normal superphosphate was once the predominant source of phosphate fertilizer. In recent years triple superphosphate and the ammonium phosphates have replaced normal superphosphate as the principal source of phosphate. However, because of its ease of preparation, normal superphosphate is still used in substantial quantities in the United States.

Basically, the preparation of normal superphosphate involves the reaction of phosphate rock with sulfuric acid to form mono-calcium phosphate. The overall reaction which occurs can be written as follows:

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 + H_2O \rightarrow 2\ CaSO_4 + CaH_4(PO_4)_2 \cdot H_2O$$

The monocalcium phosphate thus formed is water soluble and the phosphate is available for uptake by the soil solutions. No attempt is made to separate the calcium sulfate from the monocalcium phosphate.

The calcium fluoride content of the rock is also attacked by the acid with the formation of hydrofluoric acid which in turn reacts with silica in the rock to form SiF_4. The SiF_4 in turn reacts with water to form fluosilicic acid:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2\ HF_{(aq)}$$

$$4\ HF + SiO_2 \rightarrow SiF_4 + 2\ H_2O$$

$$3\ SiF_4 + 2\ H_2O \rightarrow 2\ H_2SiF_6 + SiO_2$$

However, some SiF_4 will be volatilized before it can react with the water. The amount of SiF_4 volatilized depends on the concentration of sulfuric acid used. The higher the acid concentration the more SiF_4 is evolved.

Both batch and continuous processes have been developed for producing normal superphosphate and a number of modifications of each process exist. Regardless of the process variation used, the basic process operations are the same. Figure 22 shows a flowsheet which is typical of the continuous normal superphosphate process. In the process phosphate rock containing 30-35% P_2O_5 is ground to 90%-100 mesh. The rock is fed at a controlled rate to a mixer where it is thoroughly mixed with sulfuric acid which has been diluted to about 75%. The rock-acid slurry discharges from the mixer to a pug mill where additional mixing occurs and the reaction between the rock and acid starts. From the mill the slurry discharges to a slow moving conveyor (called a continuous den) where the reaction continues and the slurry hardens to a plastic mass. Residence time on the conveyor is one to two hours. As the plastic mass leaves the conveyor it is cut into chunks. The sectioned product is then transferred to a storage area for final curing. During storage, which lasts from 2 to 6 weeks depending on process conditions, the reaction between the rock and acid approaches completion. The material hardens to a solid mass and cools. From the storage area the normal superphosphate product is fed to a pulverizer (usually a hammer mill) where it is crushed and screened.

In some cases it is desired to produce a granular product. The superphosphate can be granulated before or after curing but granulation before curing is the preferred route.

As stated earlier, some fluorine, in the form of SiF_4, is evolved during the manufacture of normal superphosphate. Air pollution control regulations require that this fluoride evolution be adequately controlled. The fluorine evolution occurs primarily in the mixing and denning operations, with a much smaller amount being released during the curing step. In practice, the mixer and den are enclosed and the fumes from the enclosures are scrubbed with water to remove the fluoride plus any acid mist and dust particles that may be present.

The fluoride evolved in the curing area is much less but it may still be necessary to control the fluoride evolution. This is done by circulating air through the storage (curing) building and then scrubbing the air with water to remove the fluoride.

Triple Superphosphate Production

Triple superphosphate has become one of the principal sources of fertilizer phosphate in the United States. Monocalcium phosphate is the principal fertilizer ingredient of triple

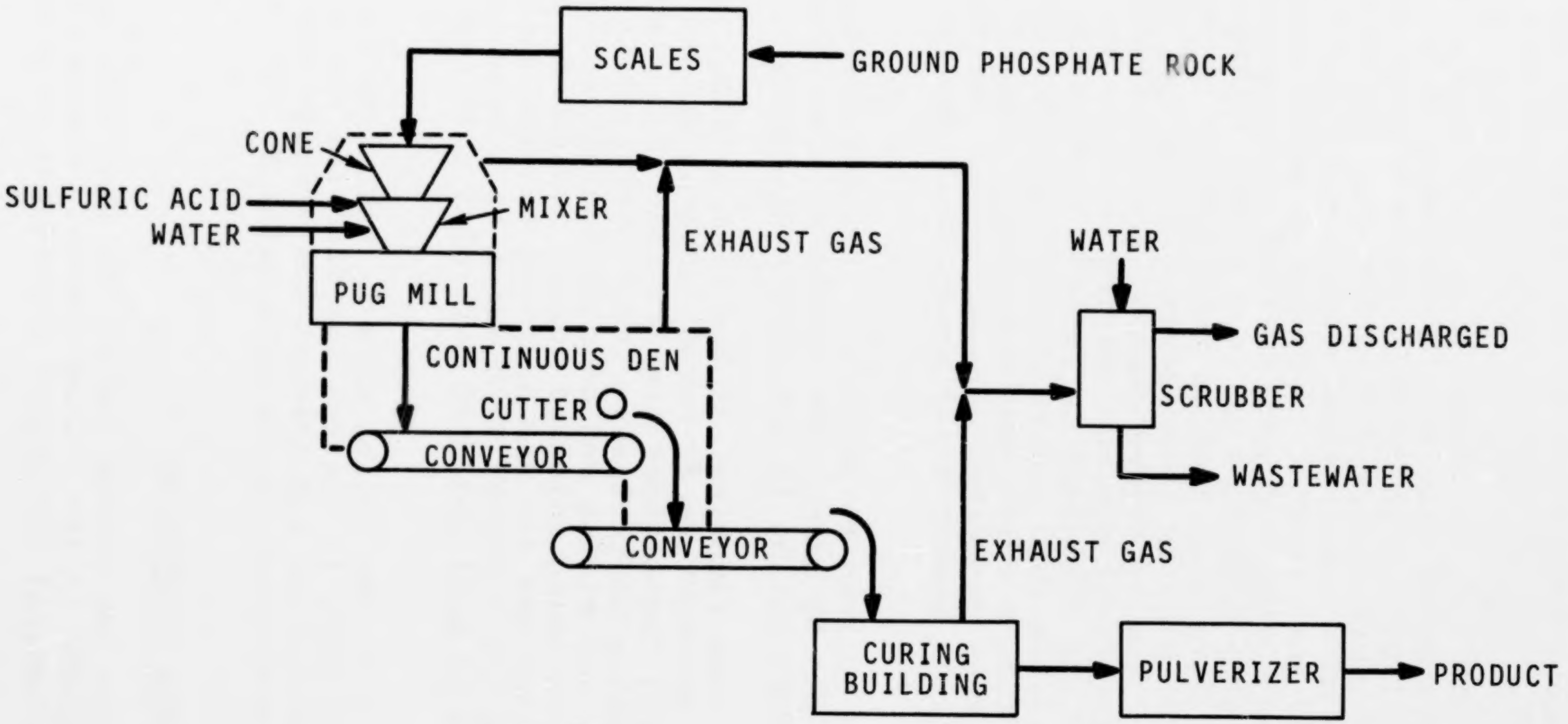

SCALES
GROUND PHOSPHATE ROCK
CONE
SULFURIC ACID
WATER
MIXER
PUG MILL
EXHAUST GAS
CONTINUOUS DEN
CUTTER
CONVEYOR
CONVEYOR
WATER
GAS DISCHARGED
SCRUBBER
WASTEWATER
EXHAUST GAS
CURING BUILDING
PULVERIZER
PRODUCT

FIGURE 22 NORMAL SUPERPHOSPHATE FLOWSHEET
(See pp 110-111 for Waste Stream Composition)

superphosphate as it is in normal superphosphate. However, as the name implies, triple superphosphate contains about three times as much P_2O_5 as normal superphosphate. This is because there is no calcium sulfate in the triple superphosphate.

Triple superphosphate is made by the reaction of phosphate rock with phosphoric acid to give soluble monocalcium phosphate. The overall reaction can be written as follows:

$$3Ca_3(PO_4)_2 \cdot CaF_2 + 14\ H_3PO_4 + 10\ H_2O$$

$$\rightarrow\ 10\ CaH_4(PO_4)_2 \cdot H_2O + 2\ HF$$

The HF formed reacts with silica to form SiF_4 which partially hydrolyzes to fluosilicic acid and partially is evolved from the reaction mass:

$$4\ HF + SiO_2 \rightarrow SiF_4 + 2\ H_2O$$

$$3\ SiF_4 + 2\ H_2O \rightarrow 2\ H_2SiF_6 + SiO_2$$

As was the case with normal superphosphate, triple superphosphate can be manufactured by either batch or continuous processes but most production is by the continuous process. Various modification of the continuous process exist but the basic operations are the same in each case. Triple superphosphate is produced as either granular or run-of-pile material.

A flowsheet typical of the production of granular triple superphosphate by the continuous process is presented in Figure 23. In the process, phosphate rock is ground to 75%-200 mesh. The ground rock is fed to a mixer where it is mixed with phosphoric acid. The resultant slurry is fed to a continuous belt where it solidifies. The discharge from the belt is crushed and sent to a storage pile for curing. Curing normally takes about 3 to 5 weeks to complete. The cured product is then sent to a pulverizer where it is ground and screened. The screened material is then sent to a granulator where it is mixed with water and steam. The resultant wet granules are discharged to an air dryer where the water is evaporated to give a hard, dense, granular product. The discharge from the dryer is screened and the product sent to storage. Oversize particles are recycled to the pulverizer and undersize to the granulator.

Evolution of fluoride, principally as SiF_4, occurs primarily at the mixer and conveyor belt, with only a limited amount occurring in the product curing area. The mixer and conveyor are enclosed; the offgases are collected and scrubbed with water to remove the fluoride.

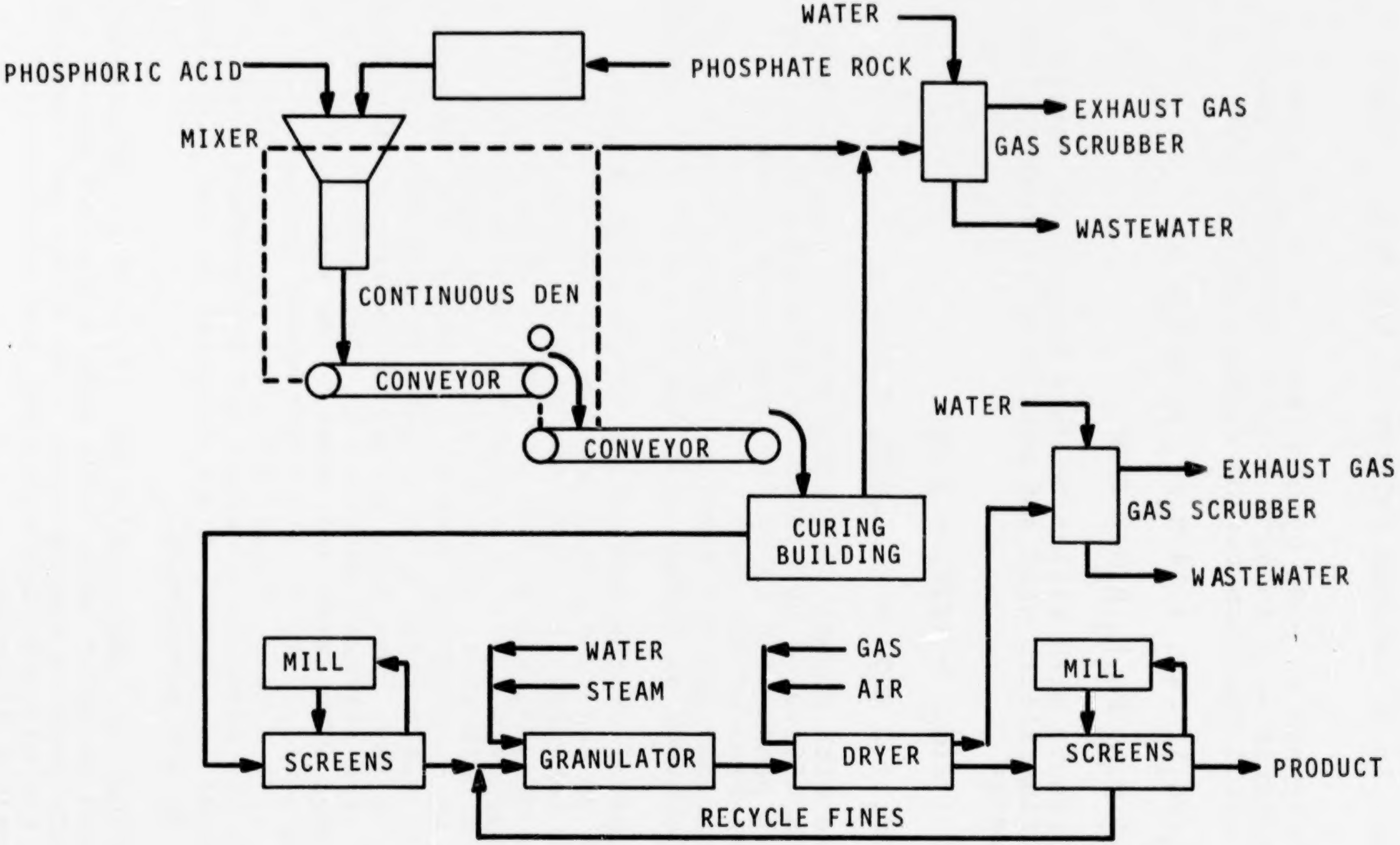

WATER
PHOSPHORIC ACID
PHOSPHATE ROCK
MIXER
EXHAUST GAS
GAS SCRUBBER
WASTEWATER
CONTINUOUS DEN
CONVEYOR
CONVEYOR
WATER
EXHAUST GAS
GAS SCRUBBER
CURING BUILDING
WASTEWATER
MILL
WATER
STEAM
GAS
AIR
MILL
SCREENS
GRANULATOR
DRYER
SCREENS
PRODUCT
RECYCLE FINES

FIGURE 23 FLOWSHEET FOR TRIPLE SUPERPHOSPHATE PRODUCTION
(See pp 111-112 for Waste Stream Composition)

The offgas from the granulator dryer also contains contaminants which must be removed before the gas is discharged to the atmosphere. This is normally done with water scrubbing.

Production of Ammonium Phosphates

The ammonium phosphates have become one of the two major sources of fertilizer phosphate. The principal advantages which lead to their increasing popularity include low production costs, good physical and chemical properties, and high analysis.

The ammonium phosphates are normally prepared by the neutralization of phosphoric acid with ammonia. The product obtained depends on the ratio of acid and ammonia used, and may be monoammonium phosphate ($NH_4H_2PO_4$), diammonium phosphate, or a mixture of the two. The diammonium phosphate product is the preferred form in the United States. The ammonium phosphates can be made from either furnace acid or wet process acid, but most ammonium phosphates intended for fertilizer use are made from wet process acid.

A variety of processes can be used to produce ammonium phosphates. The ammoniator process developed by the TVA is typical of the processes used to prepare diammonium phosphate. The flowsheet for the TVA process is shown in Figure 24. In the process, wet process phosphoric acid (about 40% P_2O_5) is partially neutralized in a reactor with anhydrous ammonia. Heat of reaction evaporates some water and a slurry forms. The slurry is pumped to an ammoniator-granulator where it is sprayed over a bed of recycled fines. More anhydrous ammonia is added in the granulator until the product has a $NH_3:PO_4$ ratio of 2:1. An excess of ammonia is required to reach the desired ratio of 2:1. In the granulator, the slurry hardens as the correct ratio is reached and a granular product is formed. The solidified diammonium phosphate product from the granulator flows to a dryer and then to screens where the oversize and undersize are removed. The oversize particles are crushed, combined with the undersize and recycled to the granulator. The product is sent to storage.

The exhaust gas from the granulator and dryer contains water and ammonia. The water which evaporates from the neutralizer also contains a substantial amount of ammonia. The ammonia in the two streams must be recovered before the gases are discharged. This is done by scrubbing the streams with the phosphoric acid which feeds the neutralizer. Scrubbing with phosphoric acid effectively removes most of the ammonia from the vapor. However, in the scrubbing operation fluoride is stripped from the phosphoric acid and released to the gas stream. A second scrubber system may be required to

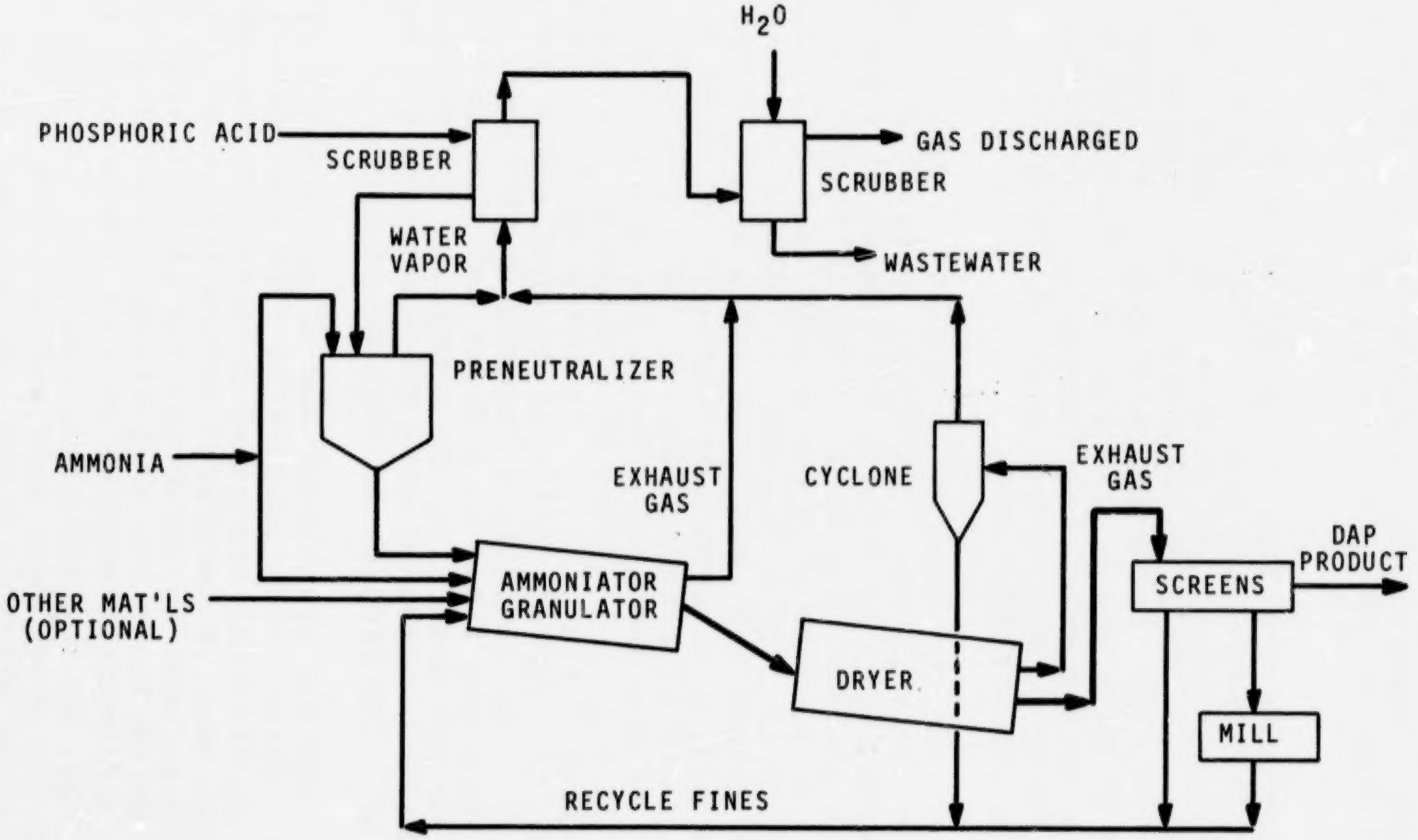

H$_2$O
PHOSPHORIC ACID
SCRUBBER
GAS DISCHARGED
SCRUBBER
WATER VAPOR
WASTEWATER
PRENEUTRALIZER
AMMONIA
EXHAUST GAS
CYCLONE
EXHAUST GAS
DAP PRODUCT
AMMONIATOR GRANULATOR
SCREENS
OTHER MAT'LS (OPTIONAL)
DRYER
MILL
RECYCLE FINES

FIGURE 24 FLOWSHEET FOR PRODUCTION OF DIAMMONIUM PHOSPHATE (DAP)

reduce the fluoride discharging to the atmosphere. A water scrubber is normally sufficient.

Ammoniated Superphosphate Production

Ammoniated superphosphates have been and still are popular fertilizers in the United States. They are produced by reacting normal or triple superphosphate with ammonia (usually in the form of an ammoniating solution) and the product composition can be varied by controlling the ratio of feed materials. In addition, it is possible to incorporate other fertilizer materials such as urea, ammonium nitrate, potassium chloride into the production scheme to make a wide range of fertilizer materials.

The reactions involved in ammoniated superphosphate production are quite complex. The overall effect is to convert the monocalcium phosphate in the superphosphate to dicalcium phosphate and the ammonia to monoammonium phosphate:

$$CaH_4(PO_4)_2 + NH_3 \rightarrow CaHPO_4 + NH_4H_2PO_4$$

Care must be taken to control the reaction since an excess of ammonia can result in the conversion of the dicalcium phosphate to insoluble tricalcium phosphate:

$$3\ CaHPO_4 + NH_3 \rightarrow Ca_3(PO_4)_2 + NH_4H_2PO_4$$

Two secondary reactions can occur if calcium sulfate is present in the superphosphate. These are:

$$NH_4H_2PO_4 + CaSO_4 + NH_3 \rightarrow CaHPO_4 + (NH_4)_2SO_4$$

$$2\ CaHPO_4 + CaSO_4 + 2\ NH_3 \rightarrow Ca_3(PO_4)_2 + (NH_4)_2SO_4$$

The first reaction is not harmful, but the second reaction is to be avoided if possible because of the insoluble tricalcium phosphate formed.

A great many variables affect the rate and extent of ammoniation. Careful consideration must be given to such factors as superphosphate particle size and moisture content, reaction time and temperature, and method of ammonia addition.(3,19,21)

Numerous processes have been developed for producing ammoniated superphosphates. They can be divided into two basic types: batch ammoniation processes with continuous cooling, drying, and screening; and continuous ammoniator processes.(3,19) The development of ammoniated superphosphate processes is closely related to the development of granular fertilizer processes. Almost all ammoniated superphosphate is produced in granular form, and the granulation techniques used are generally applicable to other products such as granular N-P-K mixtures and granular ammonium phosphates.

A typical flowsheet for production of granular ammoniated superphosphates is given in Figure 25. The process uses a rotary drum ammoniator-granulator. In the process, finely ground superphosphate (either normal or triple) is screened and fed to the ammoniator. Oversize particles are milled and recycled to the screens. In the ammoniator, the superphosphate is reacted with ammoniating solution to give a granular product. Retention time in the ammoniator is about four minutes and the reaction temperature is between 150 and 250 °F. The reaction is exothermic but it may be necessary to supply heat by adding steam directly to the ammoniator to maintain the temperature. The granular product from the ammoniator flows to a directly-heated rotary dryer where any moisture present is removed.

The dry granules are then cooled, screened and sent to storage. The undersize product is returned to the ammoniator while oversize material is milled and returned to the product stream to be rescreened.

It is necessary to control dust and fume evolution from several operations in the process. Dust is generated by the dryer, cooler, mills, and screens. Fumes evolve from the ammoniator and dryer. The fumes consist primarily of water vapor and a small amount of ammonia. The dust is collected by cyclones and returned to the granulator. Any offgas containing ammonia is scrubbed and the scrubber solution is returned to the ammoniator.

Phosphate Rock Production

Phosphate rock is the principal raw material for all phosphate fertilizer production. However, ground phosphate rock itself is sometimes used as a fertilizer under special conditions. The consumption of rock as a fertilizer is decreasing in the United States but substantial tonnages are still used. Very little processing is required to prepare the rock for use. Normally it is simply ground to -200 mesh and dried to remove the moisture. As long as the drying temperature is held below about 250 °C no gaseous fluoride contaminants are evolved. The exit gas from the dryer contains particulate matter and this is recovered by cyclones. If for any reason it is desired to calcine the rock then some fluoride will be evolved. The fluoride will be in the form of hydrogen fluoride and silicon tetrafluoride with the higher calcination temperatures favoring hydrogen fluoride evolution. The offgas from the calciner is first passed through cyclones to separate

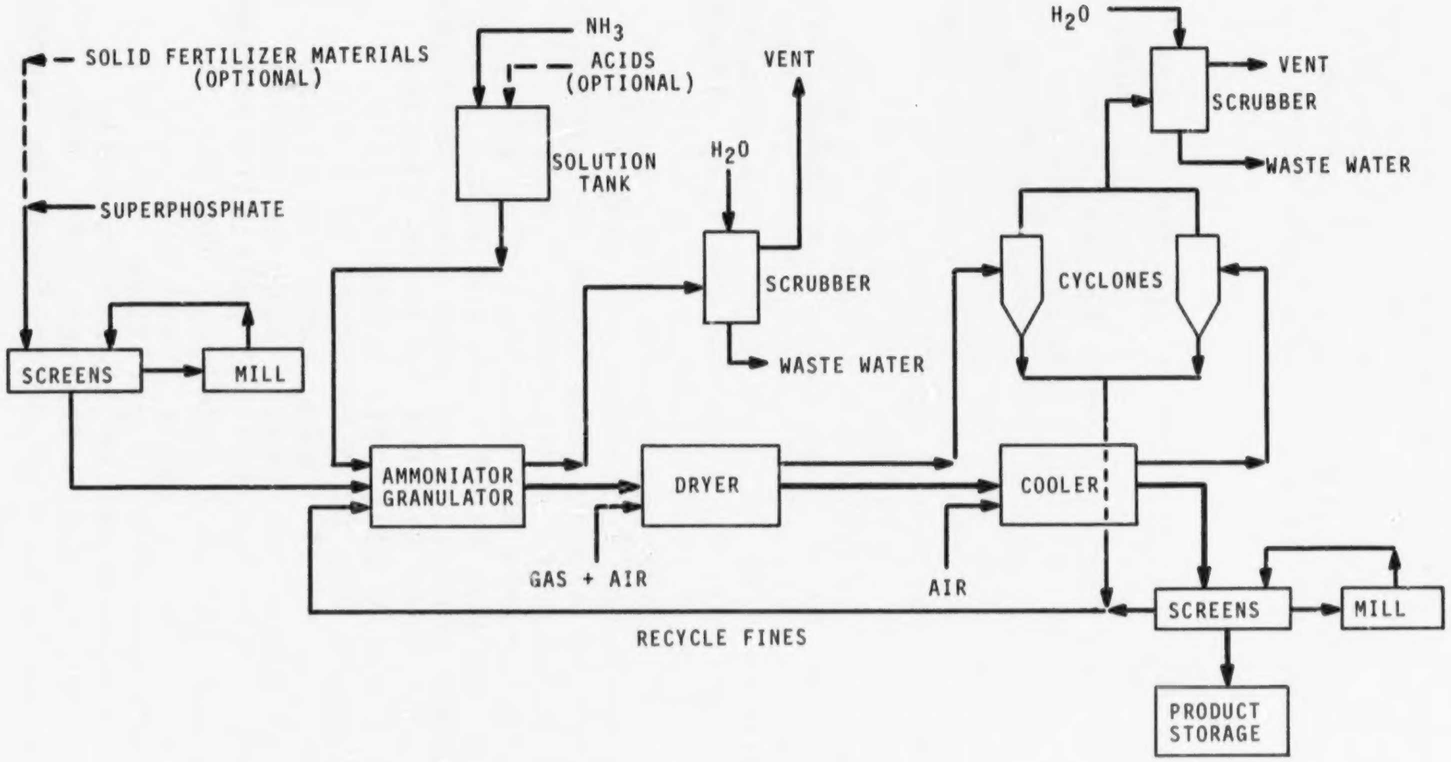

SOLID FERTILIZER MATERIALS (OPTIONAL)
SUPERPHOSPHATE
SCREENS
MILL
NH_3
ACIDS (OPTIONAL)
SOLUTION TANK
AMMONIATOR GRANULATOR
H_2O
VENT
SCRUBBER
WASTE WATER
DRYER
GAS + AIR
RECYCLE FINES
H_2O
VENT
SCRUBBER
WASTE WATER
CYCLONES
COOLER
AIR
SCREENS
MILL
PRODUCT STORAGE

FIGURE 25 AMMONIATED SUPERPHOSPHATE FLOWSHEET (Can be used for NPK Fertilizer Production)

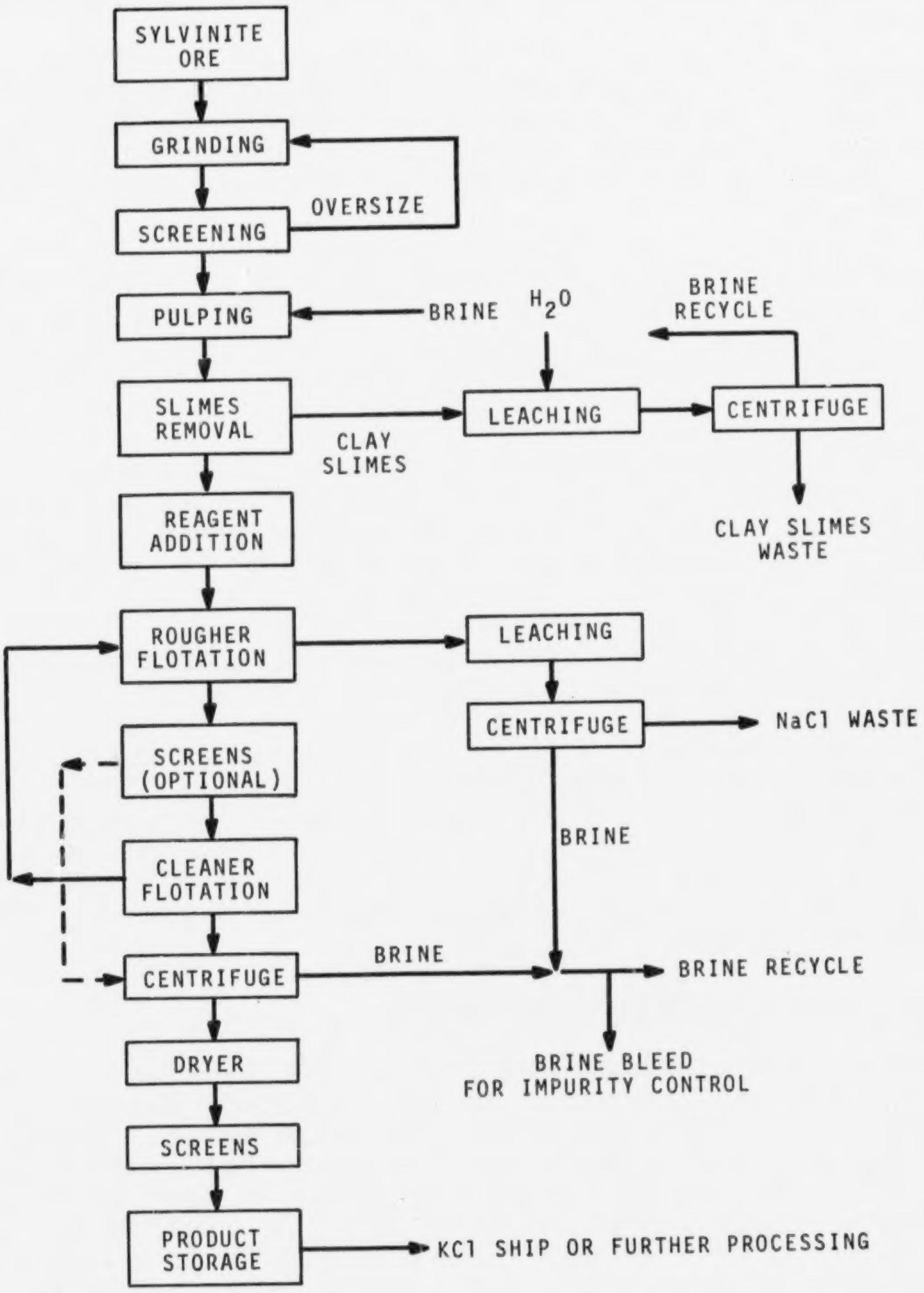
particulate matter and then scrubbed to remove the gaseous fluoride. If the fluoride is not recovered as a by-product then the scrubber solution must be disposed of.

POTASH PRODUCTION PROCESSES

The major sources of potash in the United States are natural brines and sylvinite deposits, with the sylvinite supplying approximately 90% of the potash. Flotation beneficiation and solution-recyrstallization are the principal processes used to recover KCl from sylvinite ore. Flotation plus solar evaporation is also used to recover KCl from the Bonneville, Utah brines. A complex series of solution-crystallization operations is used to recover KCl from Searles Lake brine.

Flotation-Beneficiation Process

In processing sylvinite by flotation, either the KCl or the NaCl may be floated depending on the chemical reagents used. Current practice in the United States favors flotation of the KCl.(14) The exact features of the flotation process vary somewhat among the various potash producers, depending on such factors as ore composition and end product requirements. A simplified flowsheet typical of the flotation beneficiation process (with KCl floated) is presented in Figure 26.(14,22) Typically, the coarsely-crushed slyvinite ore is sent to a grinding circuit where it is crushed and screened to give a -6 mesh fraction. Grinding to -6 mesh frees the individual KCl and NaCl particles in the ore. The -6 mesh feed is then pulped with a brine saturated with KCl and NaCl. The resulting slurry is thoroughly agitated to disperse the clay slimes and other insolubles in the ore. The sylvinite normally contains about 1% clay. The slurry is then treated in a series of screens and classifiers to remove the clay slimes and insolubles. The clarified slurry next flows to a conditioning tank where it is mixed with a depressant (starch, guar, etc.). The depressant coats any residual clay particles in the slurry so that they do not float with the KCl. Next, the slurry flows to a second conditioning tank where selective flotation agents are added. When the KCl is to be floated the flotation agents are usually aliphatic amine acetate salts.(14) Aliphatic alcohols may also be added to serve as frothing agents. From the conditioning tank the slurry flows to a primary bank of flotation cells (rougher cells) which are sparged with air. The treated KCl particles collect in the froth and are skimmed off with paddles. The KCl in the froth overflow from the rougher cells still contains substantial amounts of NaCl and other impurities. The KCl rich overflow is sent to a second set of flotation cells (cleaner cells) where the KCl is again floated off. The overflow from the cleaner cells is then centrifuged to remove



SYLVINITE ORE
GRINDING
SCREENING
OVERSIZE
PULPING
BRINE
H_2O
BRINE RECYCLE
SLIMES REMOVAL
LEACHING
CENTRIFUGE
CLAY SLIMES
CLAY SLIMES WASTE
REAGENT ADDITION
ROUGHER FLOTATION
LEACHING
CENTRIFUGE
NaCl WASTE
SCREENS (OPTIONAL)
BRINE
CLEANER FLOTATION
CENTRIFUGE
BRINE
BRINE RECYCLE
BRINE BLEED FOR IMPURITY CONTROL
DRYER
SCREENS
PRODUCT STORAGE
KCl SHIP OR FURTHER PROCESSING

FIGURE 26 TYPICAL FLOWSHEET FOR RECOVERY OF POTASSIUM CHLORIDE FROM SYLVINITE BY THE FLOTATION BENEFICIATION PROCESS (14)

the KCl from the brine and the brine is recycled. After washing, the KCl is dried, screened, and stored for shipment or subsequent processing. The KCl product is normally a light pink in color due to iron and clay contamination, and usually contains 96-97% KCl. Sodium chloride is the major contaminant.

In some processes, screens are installed between the two flotation cells and the larger KCl particles are removed. These particles are often of sufficient purity that they do not require further processing to be acceptable as fertilizer grade KCl.

The clay slimes and insolubles which are removed from the sylvinite slurry in the classifiers contains some KCl. The slurries are normally leached with a minimum of water to remove the KCl, centrifuged and discharged. The KCl-rich leach solution is recycled to the process brine system.

The underflow from the primary flotation cells contains primarily NaCl with some KCl. The underflow is heated to dissolve the KCl, centrifuged, and the solid NaCl waste discarded. The brine from the centrifuge is recycled to the process brine system.

Careful control is maintained over the water balance of the process. The major waste streams from the process are the clay slimes tailings and the salt waste. The water content of these wastes are held to a minimum by centrifuging, filtering, or settling the solids prior to discharge. Some water is lost by evaporation and is replenished by the water used to leach the clay slimes for KCl removal. In addition, it is necessary to bleed off some water from the process to remove soluble impurities. This is held to a minimum to reduce the KCl loss.

Solution-Recrystallization Process

The solution-recrystallization process for treating sylvinite ore for KCl recovery is based on the different ratios of solubility of KCl and NaCl in hot and cold water. Figure 27 shows a typical flowsheet for the recrystallization process.(14,22) The ore is first crushed to -6 mesh to free the individual NaCl and KCl particles. The crushed ore is then contacted with a recycle brine at 100 °C in a countercurrent series of dissolvers. The hot recycle brine is saturated with NaCl but unsaturated with respect to KCl. The KCl in the ore dissolves together with a small amount of the NaCl. The clay slimes in the ore are suspended in the brine. The KCl-enriched brine passes to a clarifier where the clay solids are removed. The clay solids are filtered

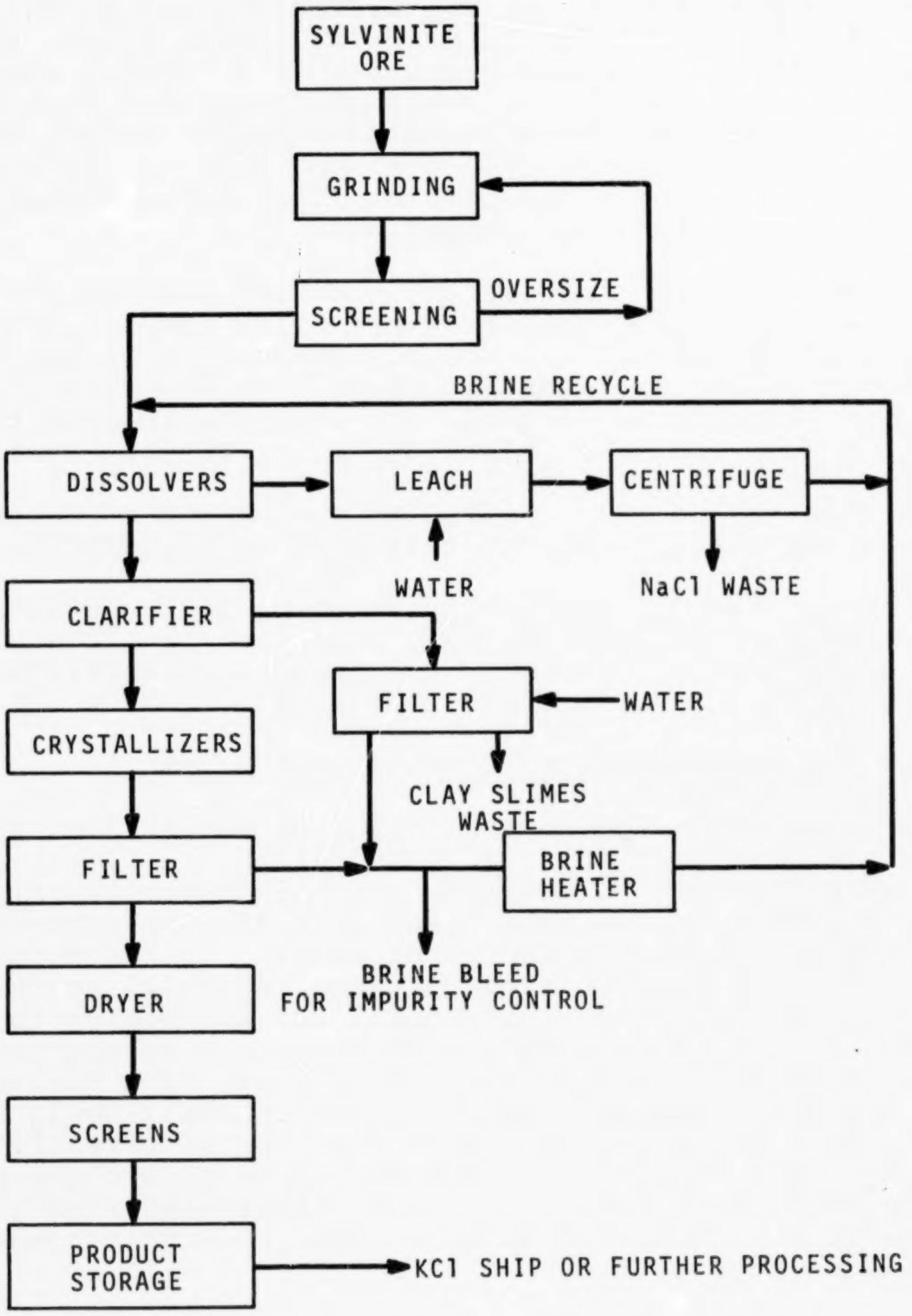

SYLVINITE ORE
GRINDING
SCREENING
OVERSIZE
BRINE RECYCLE
DISSOLVERS
LEACH
CENTRIFUGE
WATER
NaCl WASTE
CLARIFIER
FILTER
WATER
CRYSTALLIZERS
CLAY SLIMES WASTE
FILTER
BRINE HEATER
DRYER
BRINE BLEED FOR IMPURITY CONTROL
SCREENS
PRODUCT STORAGE
KCl SHIP OR FURTHER PROCESSING

FIGURE 27 TYPICAL SOLUTION-RECRYSTALLIZATION FLOWSHEET FOR RECOVERING POTASSIUM CHLORIDE FROM SYLVINITE ORE (14)

and discarded, while the filtrate brine is recirculated to the clarifier. The NaCl solids from the dissolvers are centrifuged and discarded and the brine recycled to the dissolver. The KCl-rich brine from the clarifier passes to a series of vacuum crystallizers where it is cooled and KCl crystallizes out. The KCl crystals are separated from the brine by filtration or centrifugation, washed, dried, screened, and stored. The NaCl-rich, KCl-depleted brine is reheated and recycled back to the dissolvers. The wash solution is combined with the brine and recycled.

The waste streams from process are the clay slimes, the NaCl tailings, and a bleed stream from the brine recycle system which is used to control the soluble impurities in the brine. The clay slimes and salt waste contain some KCl-rich brine. Both wastes are normally washed with water to recover the KCl and the wash solution fed to the brine recycle system. To maintain the process water balance, the water used in the wash steps is usually limited to the amount of water removed in the brine bleed and that lost by evaporation.

The quality of the KCl product produced by the solution-recrystallization process can vary depending on the NaCl content of the brine. Normally the process is controlled to give a soluble grade product (99% KCl).

Processes for Recovering KCl from Natural Brines

Recovery of KCl from the natural brine at Bonneville, Utah, utilizes a combination of solar evaporation and flotation-beneficiation.(14,22) The brine, which is a complex mixture of metal chloride and sulfates (see page 38), is concentrated by solar evaporation in a series of ponds. In the first pond the brine is concentrated with the crystallization of NaCl. Evaporation is continued until the KCl begins to precipitate. The brine is then transferred to a second pond where it is concentrated with the deposition of a mixture of NaCl and KCl. Evaporation is continued until $MgCl_2$ begins to precipitate out with the KCl in the form of carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$). The brine is then pumped to a third pond to precipitate NaCl, carnallite, and cainite ($KCl \cdot MgSO_4 \cdot 3H_2O$). The brine is next transferred to another pond to recover the remaining magnesium.

The NaCl-KCl mixture from the second pond is collected mechanically and sent to a refinery to separate the two materials. A flotation beneficiation flowsheet, similar to Figure 26, is used to recover the KCl. The process is somewhat less complex than that used to process sylvinite since the KCl-NaCl mixture is relatively pure. The precipitates from the third pond containing NaCl, $KCl \cdot MgCl_2 \cdot 6H_2O$ and $KCl \cdot MgSO_4 \cdot 3H_2O$ are washed with brackish water and the brine recycled back to the various ponds depending on composition.

The processing of Bonneville brine presents no major problems with regard to pollution since any aqueous waste stream can be recycled back to the brine source.

Recovery of KCl from the Searles Lake brine is part of a very complex series of operations designed to recover a variety of products from the brine. A number of excellent references describing the Searles Lake operation are available in the literature.(14,22,23,24) As with the Bonneville brines, pollution control is not a major problem since any aqueous waste stream can be recycled back to the brine source.

AQUEOUS PROCESS EFFLUENTS

The fertilizer industry is quite complex and a variety of types and grades of fertilizer materials are manufactured. The bulk of the aqueous waste load from the fertilizer industry, however, results from the preparation of a relatively few major fertilizer products or intermediates. Production of these materials has been analyzed based on the use of standard or typical processes. The aqueous waste streams from each process have been characterized as thoroughly as possible. The specific operations in each process which generate aqueous waste have been identified. Considerable information is available on the principal contaminants found in each waste stream and their pollutional effects.

Defining the volumes and compositions of the various waste streams is more difficult. Water recycle, minor process variations, and operating philosophies can result in a wide range of waste stream compositions and volumes for a given product between the different fertilizer plants. Wherever possible, an attempt has been made to relate the waste stream volumes to a unit quantity of product--usually on a gallons per ton basis. Normally a range of flows must be specified because of the wide variations between plants. The contaminant concentrations given for the various waste streams show the same wide range of values. In many instances it is extremely difficult to predict with any accuracy even wide ranges of waste stream volumes and composition. For example, in the cleanup of process spills aqueous waste streams are generated. It is almost impossible to quantitatively relate the volume or composition of these cleanup wastes to the fertilizer product.

In analyzing the aqueous wastes generated by the fertilizer industry one fact quickly becomes evident. The principal pollutants found in the aqueous waste from most fertilizer plants are inorganic materials. Except in a few instances, organic contaminants are relatively unimportant. Therefore, pollutional criteria such as BOD and COD are less important in evaluating fertilizer plant effluents than is the case with most industrial waste.

CLASSIFICATION OF AQUEOUS EFFLUENTS

There are in general four types of aqueous effluent streams which can be generated in a fertilizer plant:

1. cooling water
2. steam condensate

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3. process effluents
4. sanitary waste.

If any of the incoming water to the plant is purified prior to use then an additional waste stream from the purification plant may also be generated. For example, when ion exchange is used to demineralize water, regeneration of the resin bed results in waste streams with high anion or cation concentrations which must be discharged. The handling and treatment of these types of waste streams are well documented in the literature; they have not been considered in this study.

In almost any plant the sanitary waste stream is kept separate from other aqueous wastes. The problems involved in handling and treating sanitary waste from a fertilizer plant are no different from those encountered in any industrial plant. They are usually discharged to a municipal sewage system, cesspool system or an on-site sewage plant. Technology for processing sanitary wastes is well defined and has not been considered in this study.

The major portion of the water used by the fertilizer industry is for cooling purposes. This water is usually relatively low in contaminants and is usually kept separate from the more contaminated aqueous waste streams. One exception to this is in wet process phosphoric acid manufacture where cooling water is frequently combined with gypsum pond water. Unless water is readily available, it is standard practice to use cooling towers or ponds and recycle the cooling water.

The principal contaminants found in the cooling water comes from three sources: leaks in process equipment and piping; the buildup of dissolved solids from the feed water, and chemicals added to the cooling water to control biological growth, scale, and corrosion.

When cooling water is recycled using towers or ponds, natural evaporation is used to cool the water. Since the makeup water to the system always contains some dissolved solids, there will be a buildup of dissolved solids in the recirculated cooling water. Blowdown of the cooling water system is necessary to control these solids. The blowdown stream will be contaminated with not only the dissolved solids but also with the materials leaked from the process and chemical additives. The materials which leak from the process can include lubricants from pump and compressor bearings and any of the materials present in the process as feeds, intermediates, products, or by-products. The chemicals added to the cooling water can include both organics and inorganics. Chromates and phosphates are frequently added for corrosion control and organics for control of biological growth.

Another problem which must be considered in dealing with cooling water is thermal pollution. Most states place restrictions on the temperature of aqueous streams which are discharged to the environment. Means must usually be provided for cooling any aqueous waste streams which exceed the prescribed limits. When cooling water is used on a once-through basis a cooling pond is usually provided for reducing the temperature of the stream prior to discharge into surface water. The blowdown from recirculated cooling water systems is usually relatively cool and does not need additional cooling prior to discharge.

Steam condensate is another aqueous waste stream that is normally quite low in contaminants. It is usually kept separate from highly contaminated waste streams. Process equipment leaks are the principal means by which contaminants are introduced into the condensate. The condensate may or may not be recycled. When the condensate is recycled some water is lost and dissolved solids can build up unless demineralized makeup water is used. When demineralized water is used, regeneration of the demineralizer will generate a waste stream containing dissolved solids. If blowdown of the steam condensate system is necessary, the blowdown water will contain high levels of dissolved solids, materials leaked from the process, and any chemicals added to control scale formation and foaming.

On an overall industry basis, aqueous process effluents represent the major source of highly contaminated waste streams. Process water accounts for only about 20-25% of the water used by the fertilizer industry but contains the bulk of the contaminants generated by the various processes. Aqueous waste streams can normally be divided into five general classes.

1. By-product streams
2. Scrubber solutions (from gas scrubbing equipment)
3. Process spills
4. Wash solutions (from equipment cleanup)
5. Barometric condenser water.

All fertilizer processes will generate one or more of the above streams.

Despite the many different products manufactured by the fertilizer industry the number of aqueous by-product waste streams generated by the various processes are relatively few. However, the streams which are generated are usually large in volume and are highly contaminated. A typical example is the gypsum slurries resulting from wet process phosphoric acid production.

Scrubber solutions represent a sizable and growing source of contaminated water in the fertilizer industry. As air pollution control regulations become more restrictive, scrubbing of gaseous waste streams to remove pollutants becomes more prevalent. In the fertilizer industry most scrubbing operations are carried out using water or aqueous solutions. This results in the formation of aqueous waste streams which must be treated prior to discharge. The concentration of pollutants in the aqueous waste can vary over wide ranges depending on gas stream concentrations and on scrubber solution recycle. In some cases the water scrub is used on a once-through basis and the concentration of pollutants in the aqueous waste is relatively low. The stream may or may not require treatment prior to discharge. In other cases the scrub solution is recycled and the pollutant concentration can build up to high levels, limited only by the equilibrium between gas and aqueous phase concentrations. In normal operation a side stream of scrubber solution is continuously removed to control the concentration in the scrub recycle below the equilibrium level. The side stream is usually quite high in pollutants and must be treated prior to discharge. A typical example of scrub solution wastes in the fertilizer industry is the solution used to scrub fluoride-containing gaseous effluents from superphosphate reactors and dens. Recovery of fluoride from various gas streams by aqueous scrubbing represents the major source of aqueous waste streams in most phosphate fertilizer operations.

In any processing operation spills occur, regardless of the care used in process control and maintenance. These spills can be solid or liquid depending on the particular operation. It is more or less standard practice in the fertilizer industry to cleanup such spills using water or acid. The spilled material is usually washed to a sump where it can be collected for recycle to the process or subsequent discharge. The pollutants associated with spill cleanup are the product material itself, processing intermediates, or reactants. In most large, well-run processing plants, spills account for only a small percentage of the waste load (<1%). In small plants such as bulk blend or liquid mix plants, which have small processing waste loads, spills can account for a substantial portion of the total plant waste load.

In certain processing operations it is sometimes necessary to shut down various pieces of equipment for cleanup. The cleanup operation can result in the generation of an aqueous wash solution which may be contaminated with the various materials used in or resulting from the processing operation. In the bulk blend and liquid mix plants, where a variety of fertilizer formulations are produced in the same equipment, cleanup produces a major portion of the aqueous waste load for the plant. Since the wash solution is normally not recycled back to the process it must be discharged to the environment.

There are many operations in the fertilizer industry, such as evaporation, drying, or process reactions, which generate condensable gas streams--principally water vapor. These condensable gas streams frequently contain volatile contaminants such as unreacted feed materials (e.g., ammonia). If the contaminant concentrations in the condensables are high then indirect cooling is normally used for condensation. The condensate is returned to the process or treated to remove the contaminants prior to discharge. In many cases the contaminants in the condensable stream are comparatively low and a barometric condenser is used for condensation. This results in a large aqueous waste stream containing low levels of contaminants. By using a cooling tower or pond the barometric condenser water can be recycled in which case the contaminant can build up to substantial levels. If water is readily available, the barometric condenser water is normally used on a once-through basis.

AQUEOUS EFFLUENT VOLUMES AND COMPOSITIONS

In the production of the various major fertilizer materials, each process will generate one or more of the several waste streams described above. Table 4 lists the potential aqueous waste streams for each product under consideration assuming the typical processes described earlier are used. In every process, spills will occur which can lead to an additional waste stream. However, it is impossible to define the magnitude and concentrations of such streams. In a phosphate fertilizer complex, waste streams generated by spills are usually discharged to the acid plant gypsum pond where they become a part of the overall waste water system for the complex. In ammonia plant complexes the spill waste is usually combined with the other highly contaminated waste streams. The magnitude and composition of the other waste streams generated by the various processes are described in the following sections: Unfortunately, in many plants specific information on individual waste streams is not available since the individual streams are not monitored. Instead, most plants monitor only the total waste load of the combined contaminated waste stream.

TABLE 4

PROBABLE AQUEOUS WASTE STREAMS FROM FERTILIZER PROCESSING

Product	Potential Waste Streams*
Ammonia	Process condensate Cooling water Steam condensate
Ammonium nitrate	Cooling water Steam condensate Off-gas scrubber solutions Condenser water
Ammonium sulfate	Condenser water Off-gas scrubber solutions
Urea	Cooling water Steam condensate Off-gas scrubber solutions
Calcined phosphate rock	Off-gas scrubber solution
Wet process phosphoric acid	Cooling water Gypsum slurry Off-gas scrubber solution Acid sludge Steam condensate
Furnace phosphoric acid	Cooling water Sludge Phossy water Off-gas scrubber solution
Normal superphosphate	Off-gas scrubber solutions
Triple superphosphate	Off-gas scrubber solutions
Ammonium phosphate	Off-gas scrubber solutions
Ammoniated superphosphate	Off-gas scrubber solutions
Potassium chloride (sylvinite)	Recycle brine bleed Salt-slimes tailings
Potassium chloride (brine)	Recycle brine bleed Salt tailings
NPK fertilizers	Off-gas scrubber solutions
Liquid blends	Equipment washdown
Bulk blends	Equipment washdown

*Waste streams generated by spill cleanup not included

Ammonia Production

In the production of ammonia the principal contaminated waste streams are process condensates, blowdown from cooling water systems and wash solutions. Boiler water blowdown may also contribute to the waste load.

When synthesis gas is prepared by steam reforming of natural gas at high pressures, various steps in the process require cooling or quenching of the gas stream. When the gas is cooled, water condenses and the condensate must be drained from the system. Whenever possible the condensate is returned to the process. However, it is impossible to return all of the condensate to the process and that which is not recycled must be disposed of. For example, when the synthesis gas is cooled and compressed before entering the synthesis circuit a knockout pot is used to collect condensed water and oil from the gas stream, and this stream must be disposed of. The condensate streams will contain CO_2 and some monoethanolamine (an aqueous monoethanolamine (MEA) solution is used to strip the CO_2 from the synthesis gas and some MEA enters the gas stream). Any process leaks and spills and plant cleanup are normally washed to a sump system and collected. They and the process condensates are usually combined to give a single waste stream. Specific information on the individual waste stream volumes and compositions is limited. Most plants do not monitor the individual streams, but only the combined stream. Typical composition and volume ranges for the combined waste stream are presented in Table 5.

Ammonia production requires extremely large volumes of cooling water. Volume requirements are reported to range from 20,000-185,000 gallons per ton of ammonia product. For a 600 ton per day ammonia plant this corresponds to a cooling water flow of 8,000-74,000 gpm. When the cooling water is used on a once-through basis contamination of the cooling water effluent is normally not a problem, except for thermal pollution. The water is normally discharged to the receiving water without treatment except for temperature reduction.

The large volumes of cooling water required make once-through operation impractical in most cases. Normally the cooling water is recycled using cooling towers or ponds. The number of cycles of concentration that can be used depends primarily on the purity and availability of the fresh makeup water. In most cases the number of cycles of concentration will be in the range of 3-7. The volume of blowdown required to control impurities is usually in the range of 1-2% of the cooling water flow. Makeup water volume will usually be several times the blowdown volume, because of water lost by evaporation and windage in the cooling tower or pond.

TABLE 5

TYPICAL AMMONIA PLANT WASTE WATER VOLUME AND COMPOSITION*

Contaminant	mg/ℓ	Contaminant	mg/ℓ
Ammonia	20-100	BOD	50-150
CO_2	150-750	COD	60-200
MEA	50-100	Oil	100-10,000

Waste Water Volume 100-1000 gal/ton NH_3

*Does not include cooling water or boiler water blowdowns

The volume of blowdown water from an ammonia plant cooling water system can vary over a wide range and values from 200-3500 gallons per ton of product have been reported. Normally, however, the blowdown volume will run from 400-1000 gallons per ton NH_3. The composition of the blowdown water will depend on the feed water composition, cycles of concentration, process leaks, and materials added to the cooling water for corrosion, scaling and plant growth control. Typical ranges of concentration for various impurities are given in Table 6.

TABLE 6

COMPOSITION OF AMMONIA PLANT COOLING WATER BLOWDOWN

Contaminant	mg/ℓ	Contaminant	mg/ℓ
Chromate	0-300	NH_3	10-100
Phosphate	0-50	MEA	0-10
Zinc	0-30	Sulfate	500-5000
Heavy metals	0-60	TDS	500-10,000
Fluoride	0-10	BOD	10-300
Biocides	0-200	COD	15-400
Misc. organics	0-100	Oil	10-1000

Blowdown volume 400-1000 gal/ton NH_3

Ammonia production requires substantial quantities of steam and process waste heat boilers are used to generate this steam whenever possible. In some plants additional steam generation may be required. Condensate recycle to the steam boiler can lead to generation of a boiler water blowdown waste which is high in dissolved solids and corrosion and scale inhibitors.

Ammonium Nitrate Production

In the production of prilled ammonium nitrate there are various operations which can result in the generation of gas streams which can contain ammonia or nitrate ion or both. These operations include the neutralizer, where both ammonia and nitric acid may be vaporized, the concentrator, and the prilling tower. Normally scrubbing is required to remove the nitrogen species from the gas streams. Water scrubbing is usually used and the scrub water may or may not be recycled. The ammonia and nitrate recovered in the scrub system is normally not returned to the process. The volume of nitrogen containing waste water generated is difficult to define because of the many operating variables involved. However, ammonia losses can run as high as 1% or about 4 pounds per ton of NH_4NO_3 product. Nitrate losses are usually much less.

Significant quantities of cooling water may be required in ammonium nitrate production (up to 35,000 gallons per ton of product). When large volumes are required cooling water recycle is usually used. This means cooling water blowdown is required. The volume of blowdown required will depend primarily on makeup water purity. The composition of the blowdown stream will be quite similar to that generated in ammonia production, except that there will be a significant nitrate concentration in the blowdown from ammonium nitrate production.

Process spills and resultant cleanup can generate a significant waste stream. Solid spills are usually recovered if possible. Liquid spills, however, are usually washed to a sump or drainage system. Normally the wash solutions are not returned to the process because of the possibility of oil or grease contamination and its resultant hazard.

Ammonium Sulfate Production

In the direct production of ammonium sulfate, ammonia and sulfuric acid are reacted in a crystallizer to form the sulfate. Heat of reaction causes the evaporation of water from the crystallizer solution and a loss of ammonia and sulfate. The ammonia normally must be removed from the gas stream prior to discharge. This can be done using a water scrubber, barometric condenser, or noncontract condenser. Where a water scrubber or barometric condenser is used, a water flow of 1-5 gallons per minute per daily ton of product is required. For a 300 ton per day plant this will correspond to a water flow of 300-1500 gpm. If the water is used on a once-through basis the ammonia concentration will vary between 10-100 mg/ℓ dpending on the crystallizer design. (The sulfate concentration will be less.) If the water is recycled the ammonia concentration will be much higher. Where indirect condensation is used the water and ammonia condense to give a stream which can be returned to the process.

The offgas from the ammonium sulfate dryer contains ammonium sulfate particles and small amounts of ammonia. The particulates are collected by dry means such as cyclones and returned to the process. Depending on local regulations, recovery of the ammonia from the gas stream may or may not be necessary. When recovery is required water scrubbing is used. The ammonia concentration in the scrub solution is quite low. If water is used on a once-through basis scrub volumes vary from 60-600 gallons per minute for a 300 ton per day plant. The ammonia concentration is usually less than 10 gm/ℓ.

Process spills are usually washed to a retention sump with a minimum of water. Frequently the liquor from the sump is used as the wash solution. The sump liquor is normally returned to the process.

Urea Production

There are several possible aqueous waste streams which may be generated in a urea plant. They include cooling water or cooling water blowdown, steam condensate or blowdown, and waste water used to scrub ammonia from offgas streams.

The production of urea can require large volumes of water for cooling. Values from 0-85,000 gallons per ton of urea have been reported. Most plants, however, use 10,000-40,000 gallons per ton of product. The once-through urea processes require the least amount of cooling, while total recycle processes require the largest volumes. Normally the volumes of cooling water required make once-through cooling water use impractical. When once-through cooling is used, however, the impurities in the effluent water are low. Treatment prior to discharge is normally not required except for ponding to reduce the temperature. The cooling water is normally kept separated from other waste streams. When the cooling water is recycled impurities build up and blowdown is required. As in any cooling water recycle system the number of cycles of concentration is normally determined by the purity and availability of the feed water. The number of cycles of concentration used in urea production usually varies from 3-7 as in most recycle cooling water systems. The concentrations of impurities in the blowdown stream can vary over wide ranges but will be quite similar to those given for the blowdown from ammonia plant cooling water systems. The only significant difference is that urea plant blowdown streams will contain small amounts of urea (up to 50 mg/ℓ), and little or no MEA. The volume of the blowdown stream can vary from 50-2000 gallons per ton of product with the usual range being 200-800 gallons per ton.

Urea production requires significant volumes of steam (up to 8,000 pounds per ton of product). Steam condensate used on a once-through basis presents no disposal problem since the condensate is very low in contaminants. Blowdown from recycle boiler water systems can be a problem. Normally 10-20 cycles of concentration can be used because treated makeup water is usually used. Boiler water blowdown will normally amount to 5-10% of the boiler water. The blowdown volume will range from 20-100 gallons per ton of urea. The typical range of impurity concentrations are shown in Table 7.

TABLE 7

COMPOSITION OF UREA PLANT BOILER WATER BLOWDOWN

Contaminant	mg/ℓ	Contaminant	mg/ℓ
Phosphate	5-50	EDTA	0-50
Zinc	0-10	Misc. organics	0-200
Heavy metals	0-10	TDS	500-3500
Sulfite	0-100	Alkalinity	50-700
Suspended solids	50-300	Hardness	50-500

Several gas streams are generated in urea production which can contain ammonia. Air pollution regulations may require that these gas streams be scrubbed for ammonia removal prior to discharge. In the total recycle process inert gases build up in the recycle system and must be purged. The purge stream will contain small amounts of ammonia and carbon dioxide. The urea solution from the last decomposer stage will contain small amounts of ammonia and possibly carbon dioxide. In the concentrator this ammonia will be evolved with the water vapor. In addition, any biuret formed will result in additional ammonia release. Ammonia can also be released due to hydrolysis of urea in the concentrator. As a result, the vapor stream from the concentrator can contain significant quantities of ammonia. Ammonia releases as large as 3-4 pounds per ton of product are possible. Additional ammonia release is possible in the prilling towers and the air stream exiting the prilling tower may contain small amounts of ammonia. When the ammonia loss is high, as from the concentrator, ammonia recovery and recycle to the process is possible. However, even when ammonia recovery is practiced, considerable ammonia containing waste volumes may still be generated due to gas scrubbing requirements.

Process spills can generate significant volumes of waste water. Wash solutions used to clean up spills are usually combined with other contaminated waste streams and not recycled to the process.

Little information is available on the individual contaminated waste streams from urea production since most plants do not analyze the individual streams. Compositions of the combined waste streams (exclusive of cooling water and boiler water blowdown) are available and typical compositions and volumes are presented in Table 8.

TABLE 8

TYPICAL UREA PLANT WASTE WATER VOLUME AND COMPOSITION*

Contaminant	mg/ℓ	Contaminant	mg/ℓ
Ammonia	200-4000	Oil	10-100
Urea	50-1000	BOD	30-300
CO_2	100-1000	COD	50-500

Volume 50-2000 gal/ton urea

*Does not include cooling water and boiler water blowdown

Aqueous Wastes From Nitrogen Fertilizer Plant Complexes

The aqueous process waste streams generated by the productions of nitrogen fertilizers are quite similar in composition. In industrial complexes where two or more of the nitrogen fertilizers are produced the aqueous process wastes are usually combined and handled as a single stream for treatment and disposal. Table 9 summarizes the typical range of compositions and volumes of the individual waste streams which could be encountered in a nitrogen fertilizer production complex. Cooling water and boiler water blowdown may also be combined with the process waste streams after chromate removal, but have not been included in the numbers given in Table 9.

Phosphate Rock Calcination

When phosphate rock is calcined, fluoride is evolved. The evolved species are silicon tetrafluoride and hydrogen fluoride. The ratio of HF to SiF_4 increases as the calcining temperature is increased. Even at low calcination temperatures, however,

TABLE 9

COMPARISON OF AQUEOUS PROCESS WASTE STREAMS FROM NIGROGEN FERTILIZER PLANTS

	Aqueous Process Waste Streams*			
	Ammonia Plant	Ammonium Nitrate Plant	Ammonium Sulfate Plant	Urea Plant
Volume (gal/ton product)	100-1000	50-1200	100-10,000**	50-2000
Contaminants (mg/ℓ)				
NH_3	20-100	200-2000	10-1000**	200-4000
CO_2	150-750			100-1000
NO_3^-		50-1000		
$SO_4^=$			5-500**	
MEA	50-100			
Urea				50-1000
Oil	100-10,000			10-100
BOD	50-150	<20	<20	30-300
COD	60-200	<20	<20	50-500

* Does not include cooling water and boiler water blowdown

** Wide range due to possible recycle of aqueous scrubber solutions hydrogen fluoride is the principal fluoride species. The amount of fluoride evolved depends on the calcining temperature, and Figure 28 shows typical fluoride evolution as a function of temperature. Fluoride evolution does not begin below about 250 °C and the rock must be fused to remove more than 90% of the fluoride.

The fluoride evolved is scrubbed with water or dilute hydrofluoric acid. Since very little SiF_4 is normally present, the scrubber product is principally hydrofluoric acid:

$$HF_{(g)} + H_2O \rightarrow H_3O^+ + F^-_{(aq)}$$

To effect the required fluoride removal a small flow of fresh or neutralized scrubber water must be used in the final stage of the scrubber. Recycle scrub solution can normally be used in the first stage of scrubbing. If gypsum pond water is available this can be used for scrubbing. If pond water is not available (or recovery of the fluoride is desired) the scrub water is recycled. The concentration of hydrofluoric acid in the scrub solution builds up, and a bleed stream is required to maintain the acid concentration at an acceptable level. The maximum acceptable acid concentration will depend on a number of factors; primarily gas stream fluoride concentration and scrubber design.

The bleed stream can be used to recover salable fluoride products. If not, then the bleed stream must be treated for fluoride removal prior to discharge.

The total fluoride evolved will depend on the calcining conditions. For a 3.5% rock the maximum fluoride evolution would be 65-67 pounds per ton of rock treated. Fusion would be required to release this amount of fluoride.

Wet Process Phosphoric Acid Production

In the production of wet process phorphoric acid by the dihydrate process the gypsum by-product ($CaSO_4 \cdot 2H_2O$) represents a major disposal problem. The quantity of gypsum formed is about 1.5 tons per ton of rock processed which corresponds to about 4.5-5 tons per ton of P_2O_5 product.

In a few cases the gypsum from the acid plant filters is slurried with water and pumped into the ocean for disposal. Usually, however, the slurried gypsum is pumped to a holding pond (normally called a gypsum pond) where the gypsum settles out to give a clear supernate. The gypsum pond usually is a diked area which may be several hundred acres in area.

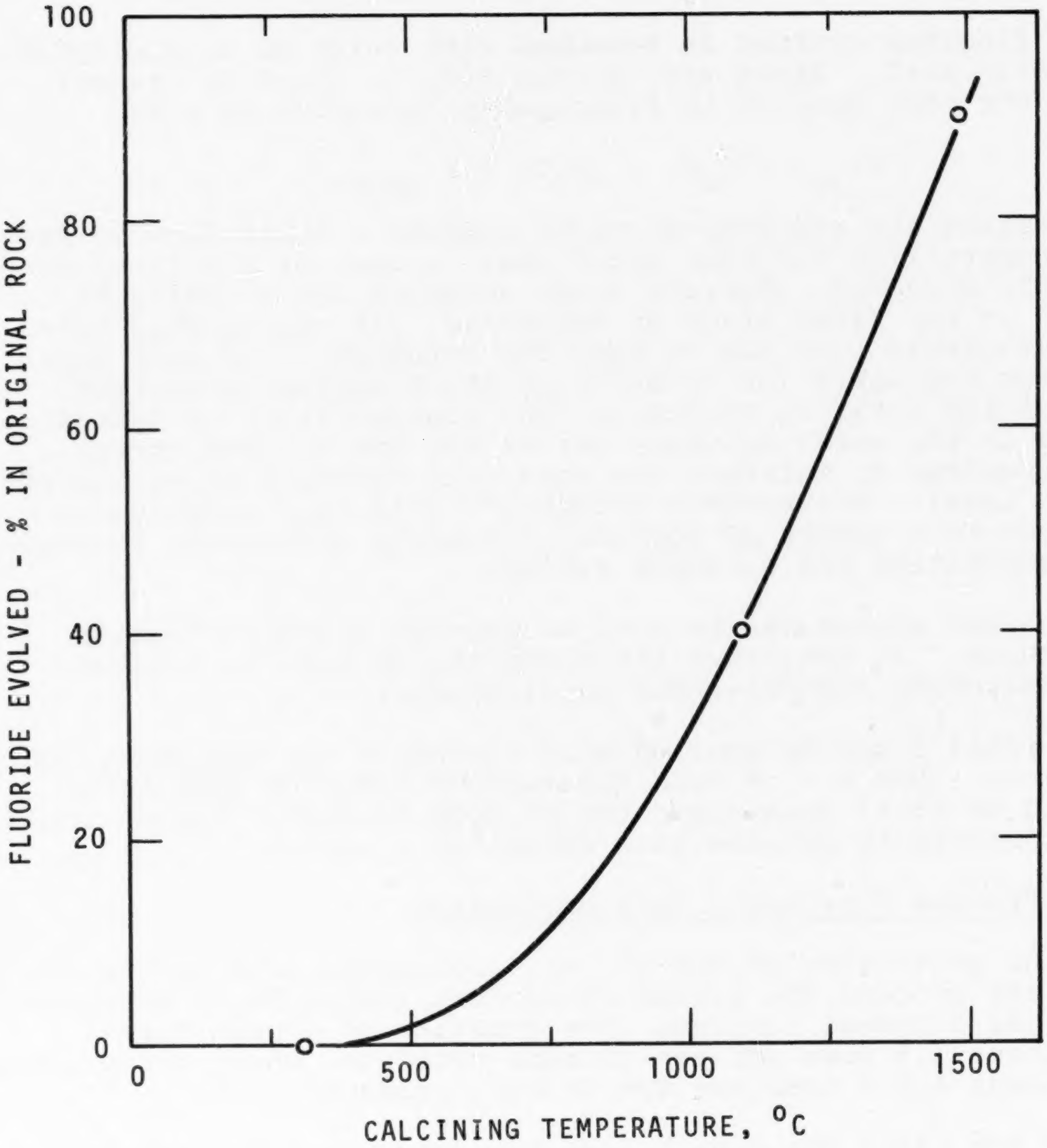

FIGURE 28 FLUORIDE EVOLUTION DURING CALCINATION OF PHOSPHATE ROCK

Two general rules of thumb are that (1) the pond area should be at least 0.5 acres per daily ton of P_2O_5 production, and (2) the deposited gypsum accumulates at the rate of about one acre-ft per year per daily ton of P_2O_5. Normally all the contaminated waste streams in the acid plant are fed to the gypsum pond. In phosphate fertilizer complexes the waste stream from other processes are usually discharged to the gypsum pond as well. The clear supernate from the gypsum pond is recycled back to supply most of the water requirements for the acid plant and other processes. In well-run acid plants recycled pond water supplies over 80% of the gross water requirements of the plant. As the pond water is recycled, dissolved impurities build up until an equilibrium composition is reached. The typical range of concentrations for the principal impurities in the pond water (at equilibrium) are given in Table 10. During periods of heavy rainfall the pond water composition may vary somewhat, but not to any great degree.

TABLE 10

TYPICAL EQUILIBRIUM COMPOSITION OF GYPSUM POND WATER

Contaminant	Concentration, mg/ℓ
P_2O_5	6000-12,000
Fluoride	3000-5000
Sulfate	2000-4000
Calcium	350-1200
Ammonia	0-100
Nitrate	0-100
pH	1.0-1.5

Some fresh makeup water is required for certain process operations such as cooling compressors and cooling the tank where the sulfuric acid is diluted prior to entering the digestor. The trend, however, is to reduce fresh water requirements to a minimum.

In areas with little rainfall the evaporation of water from the gypsum pond area makes the discharge of pond water to the environment unnecessary. In most areas some pond water must be discharged. The discharge volume is normally dependent on rainfall and will vary widely during different times of the year for a given plant. In some localities, such as Florida, the volume of water discharged from the pond is very close to the volume of rainfall collected in the pond during the rainy season. Discharge from the pond of a 600 ton P_2O_5/day acid plant can run as high as 5000 gpm during periods of high rainfall. Over a year period the discharge should average 500-1000 gallons/ton of P_2O_5. In many acid plants the gypsum pond discharge is the only plant waste stream requiring treatment.

The soluble fluoride in the pond water, at equilibrium, will have a significant partial pressure. Slack(20) reports the following values:

$$p\,SiF_4 \cong 0.00007 \text{ mm Hg}$$

$$p\,HF \cong 0.0008 \text{ mm Hg}$$

This results in a considerable loss of fluoride to the atmosphere on windy days (up to 200 pounds per day from a typical gypsum pond). However, the fluoride concentration in the air is only about 1 ppb.

Large volumes of cooling water are required in wet process phosphoric acid production. Fresh or salt water is sometimes used for cooling on a once-through basis, and the discharge water contains very few contaminants. The water is usually discharged to the receiving water without treatment, except for cooling and pH monitoring. In most cases the cooling water is recycled, and in most plants the gypsum pond water is used for most cooling purposes. Fresh water for cooling is restricted to certain specific purposes as mentioned earlier. In some plants the cooling water circuit is kept separate from the pond water circuit. Cooling ponds or towers are used, the cooling water is recycled, and only the cooling water blowdown is sent to the gypsum pond.

Because of its pH and composition, the gypsum pond water is quite corrosive and special materials of construction are required when the pond water is used for cooling.

When phosphate rock is reacted with sulfuric acid to make phosphoric acid the fluoride in the rock is also attacked by the acid and freed. The distribution of the fluoride between the various process streams can vary significantly depending on the equipment design used. Table 11 shows the fluoride distribution normally encountered in the dihydrate process.

TABLE 11

FLUORIDE DISTRIBUTION IN WET PROCESS PHOSPHORIC ACID PRODUCTION

	% of Total Fluoride in Rock			
Fluoride Disposition	Typical Range	Typical Values		ERCO
Evolved from Reactor and Filters	4-7	5	5.5	5
Evolved from Concentrator	35-45	40	41.9	60-65
Remaining in Gypsum	25-30	30	27.8	20-25
Remaining in Acid Product	20-30	25	24.8	10
Reference	(20)	(26)	(20)	(27)

Air pollution control regulations require that the fluoride evolved from the reactor, filters, and concentrator be removed before the gas stream is discharged to the atmosphere. The fluoride is usually scrubbed from the gas streams using water or dilute fluosilicic acid. When the fluoride concentration in the gas stream is high, as in the water vapor-fluoride stream from the acid concentrator, surface condensers are sometimes used. The fluoride is evolved as silicon tetrafluoride and hydrogen fluoride. Silicon tetrafluoride is the predominant species in the vapors from the reactor and filters. The vapor from the concentrator contains both HF and SiF_4.

When silicon tetrafluoride is scrubbed it reacts with the water to form fluosilicic acid and silica:

$$3\ SiF_4 + 2\ H_2O \rightarrow 2\ H_2SiF_6 + SiO_2$$

When a mixture of SiF_4 and HF is scrubbed the HF and SiF_4 combine in the scrub medium to form H_2SiF_6 but no silica is formed if the $HF-SiF_2$ ratio is 2:1. If the ratio is greater than 2:1 free HF is present in the scrub solution. If the ratio is less than 2:1 some silica is formed.

If the fluoride is not to be recovered for sale, gypsum pond water is used to scrub the fluoride from the gas stream. The scrubber solution recycles to the gypsum pond and accounts for a major portion of the fluoride that builds up in the pond water system. Fluoride recovery in the scrubbers usually exceeds 95% and in some localities air pollution control regulations make greater than 98% recovery necessary. The partial pressure of SiF_4 and HF in the pond water makes it difficult to reach these recovery levels and scrubber design can be quite complex. In some instances a small fresh water stream is used in the final stage of scrubbing to reduce the fluoride in the exit gas to an acceptable level. This stream is then used for earlier scrubbing stages, or is sent directly to the gypsum pond.

A great deal of effort has gone into the development of suitable fluoride scrubbers and a number of references on scrubber design are available in the literature.(28,29,30,31)

When economics dictate, fluoride may be recovered as fluosilicic acid for sale or for conversion to other fluoride products. (See Chemical and Engineering News - April 19, 1971 - p. 18 for a discussion of U.S. fluoride market.) When recovery is practiced the fluoride is scrubbed from the gas stream using a dilute solution of fluosilicic acid. The acid solution is recycled and the concentration can build up as high as 25% H_2SiF_6. A continuous side stream is removed from the recycle system as product to maintain the acid concentration at the desired level. Normally, a two stage scrubber system is used since the recycle acid solution will not reduce the fluoride in the exit gas to the desired level. The fluosilicic acid solution is used in the first stage scrubbing and pond water or fresh water is used in the second stage. Fluoride recovery for sale is usually practiced on the gas stream from the concentrator. In most cases greater than 80% of the fluoride is recovered for sale from the gas stream, and most of the remaining fluoride enters the gypsum pond water system.

The fluoride concentration in the gas stream from the reactor and filters is quite low and fluoride recovery is less practical. When recovery is practiced the fluosilicic acid concentration in the scrubber solution rarely exceeds 10%. Overall fluoride recovery for sale is normally less than 50% of that in the gas stream.

The product acid (52-55% P_2O_5) from the concentrator normally contains 1-3% precipitated solids, principally calcium sulfate and metal fluosilicates. With time, additional precipitates form which consist primarily of complex metal phosphates. They usually amount to about 2-5%. On storage these precipitates settle out to form a sludge.

When the phosphoric acid is used on site the sludge does not present a problem and is usually not removed from the acid. When the acid is to be shipped, however, the sludge can be a major problem since it can accumulate in shipping containers or interferes with the customer's use of the acid.

Washing of the sludge from the shipping containers can create a significant waste stream. Some plants attempt recovery of the sludge from the wash solutions, but normally it is discharged to the gypsum pond if one is available.

The preferred approach when acid is to be shipped is to store the acid in tanks for a substantial period of time. The sludge settles out and is removed as an underflow from the tanks by means of rakes. The recovered sludge, which contains substantial amounts of phosphate, is usually disposed of by blending into a fertilizer, usually triple superphosphate.

Significant quantities of steam are used in wet process phosphoric acid production. In many plants the steam is used on a once-through basis. Uncontaminated steam condensate is discharged to the receiving waters without treatment. Steam condensate which is contaminated, such as that from barometric condensers, and vacuum ejectors, is discharged to the gypsum pond. When steam condensate is recycled only the uncontaminated portion is returned to the steam plant.

In the phosphoric acid plant spills occur and they are usually cleaned up by washing to a sump system from which they are moved to the gypsum pond.

Furnace Phosphoric Acid Production

The principal waste stream generated in the production of furnace grade phosphoric acid is a waste water stream contaminated with elemental phosphorus, called phossy water. The phossy water can originate from three principal points in the process: phosphorus condensers, the phosphorus storage area, and phosphorus sludge handling.

The elemental phosphorus vaporized from the electric furnace passes through dust collectors and is then condensed with water in one or more condensers. The resulting mixture of liquid phosphorus and water is collected in a sump. The liquid phosphorus settles to the bottom of the sump, while the water forms a cover layer over the phosphorus. Water from the cover layer is recycled back to the condenser system. Impurities will build up in the water and a bleed is necessary to control the impurity level. The impurities consist principally of colloidal phosphorus particles and soluble fluoride scrubbed out of the gas stream in the condenser.

When the phosphorus is condensed, most of the phosphorus collects in a relatively pure form. However, some of the phosphorus collects in a heterogeneous mixture called phosphorus sludge, which is composed of phosphorus, water and inorganic solids. About 5-10% of the phosphorus produced ends up in the sludge.

As a general rule, about 5% sludge is produced for every 1% of inorganic solids in the condensed phosphorus.(20) The solids in the sludge are composed of 40-60% SiO_2, 5-15% CaO, 2-4% Fe_2O_3, 1-3% Al_2O_3, and 2-5% P_2O_5. They will normally amount to between 1 and 5% in the crude phosphorus.(20) The sludge can be separated from the clean phosphorus by gravity difference. When this is done the separated sludge is diluted with water and sent to a centrifuge to separate the contained phosphorus. The water discharged from the centrifuge is a second source of phossy water.

The liquid phosphorus is stored under water to prevent oxidation. When the phosphorus is moved, water must be added to or removed from the storage tanks. This water is contaminated with phosphorus and is the third potential source of phossy water.

Usually, the various sources of phossy water are combined and handled as a single waste stream. The composition and volume of the phossy water can vary significantly. Typical range of compositions and volume are shown in Table 12.

TABLE 12

TYPICAL PHOSSY WATER COMPOSITION AND VOLUME

Contaminant	mg/ℓ	Contaminant	mg/ℓ
Phosphorus	1000-2000	Fluoride	100-1000
Phosphate	50-500	Suspended Solids	2000-4000

pH 3-6

Volume 1000-2000 gal/ton P_2O_5

When slag is tapped from the furnace, some fluoride, P_2O_5, and SO_2 may be evolved from the molten slag. If the slag is air cooled the evolution of gas is quite low, amounting to about one pound of total fluoride, SO_2 and P_2O_5 per ton of P_2O_5. When the slag is water quenched fluoride evolution increases and amounts to about 2.5 pounds of fluoride discharge per ton of P_2O_5 product. If the slag is treated to expand it, the fluoride evolution will increase to about 8 pounds per ton of P_2O_5 product.(32) When the slag is air cooled scrubbing of the fumes may not be necessary. In other cases, scrubbing will usually be required in order to meet air pollution control regulations. Fluorides are usually scrubbed from the fumes with water; and the water discharging the scrubber can contain up to several thousand ppm fluoride and P_2O_5 if the scrubber water is recycled.

Preparation of the phosphate rock for charging to the furnace may require agglomeration by calcination. This can lead to the generation of a fluoride-containing gas stream which must be scrubbed for fluoride removal. The scrubbing operation and waste stream generated are similar to those discussed in the previous section on phosphate rock calcination.

The preparation of phosphoric acid via elemental phosphorus requires large volumes of cooling water (25,000-45,000 gallons per ton P_2O_5 produced). If water is readily available it can be used on a once-through basis. The once-through cooling water effluent is normally low in impurities and can be discharged to the receiving waters without treatment except for reduction of the temperature to an acceptable level.

When water is in limited supply the cooling water must be recycled. The accumulation of impurities requires a periodic blowdown of the cooling water. The cycles of concentration used normally range from three to seven depending on the purity of the makeup water. The composition of the blowdown water can vary over wide ranges. Typically, the range of impurities in the water are as shown in Table 13.

TABLE 13

COMPOSITION OF FURNACE GRADE PHOSPHORIC ACID PLANT COOLING WATER BLOWDOWN

Impurity	mg/ℓ	Impurity	mg/ℓ
Fluoride	10-500	SO_2	10-100
Phosphate	10-1000	TDS	500-10,000
Sulfate	500-5000	Oil	0-10
Chromate	0-100	Other Organics	0-100
Heavy metals	0-20	Suspended solids	50-200
NH_3	0-5	pH	5.5-6.0
Nitrates	0-5		

Cooling water blowdown volume 250-1000 gal/ton P_2O_5

Normal Superphosphate Production

In the production of normal superphosphate gaseous fluorides (principally silicon tetrafluoride) are evolved from various steps in the process. The principal points of fluoride evolution are the mixer, den, and storage area. Overall fluoride evolution will vary between 10-50% of the fluoride in the rock. Assuming a 3.5% fluoride concentration in the rock, the fluoride evolved will be between 4-20 pounds per ton of product. The amount of fluoride evolved will depend primarily on the concentration of the sulfuric acid used. The higher the acid concentration the greater the fluoride evolution. The average fluoride evolution is about 35% or approximately 14 pounds per ton of product for a rock containing 3.5% fluoride. Typically, the fluoride initially in the rock would be distributed as follows:

Fluoride Disposition	% of Fluoride in Original Rock
Evolved in mixer	2
Evolved in den & conveyors	30
Evolved in storage (curing)	3
Retained in product	65

The fluoride concentration in the offgas streams from the mixer den and conveyors is relatively high, and they are usually combined and scrubbed in a single scrubber system. The gases evolved in the storage building are usually removed from the building by air circulation. The fluoride concentration in the air stream is normally quite low making fluoride removal by scrubbing impractical. Recent improvements in building design reduces the air flow required and has made scrubbing for fluoride removal practical.(20)

The fluoride is scrubbed from the gas stream with water or dilute fluosilicic acid. Some particulate matter is present in the offgas and it plus the silica formed by the reaction of SiF_4 and water complicate scrubber operation.

It is difficult to define the composition of the solution exiting the scrubber. Scrubber design, water source, and ultimate fluoride disposal all affect the type and volume of scrub solution used. When the normal superphosphate plant is operated in conjunction with a wet process phosphoric acid plant gypsum pond water can be used as the scrub solution which is then recycled back to the pond after use. In some instances a small fresh water scrub, low in fluoride, is used in the final scrub stage to reduce the fluoride in the exit gas to an acceptable level. This stream also recycles to the gypsum pond or is used in first stage scrubbing.

When pond water is not available, then a holding system is necessary so the scrub liquor can be recycled (normally the scrub water cannot be used on a once-through basis because of the potential for fluoride contamination of water supplies). The concentration of fluosilicic acid in the recycle water is allowed to build to substantial levels. Makeup fresh water is used in the last stage of scrubbing. The acid solution can be recovered for sale as 20-25% fluosilicic acid.

When the acid is not recovered for sale a fraction of the recycle liquor must be bled off to maintain the fluosilicic acid concentration. The makeup fresh water replaces the acid removed as a bleed or for sale. The bleed stream represents the principal aqueous effluent from the normal superphosphate plant which operates independent of an acid plant. This stream will carry from 4-20 pounds of fluoride per ton of product. The concentration of fluoride in the stream can vary over a widerange depending on the scrubber design but normally will be at least several percent. The volume can vary from 10-200 gal/ton of product. By treating the bleed stream for fluoride removal it can be recycled as makeup water or released to the environment.

Ammonium fluoride solution can also be used for fluoride scrubbing.(33) The silicon tetrafluoride reacts with the ammonium fluoride to form ammonium fluosilicate:

$$SiF_4 + 2\ NH_4F \rightarrow (NH_4)_2SiF_6$$

The process has the advantage that no silica is formed. However, the process has not been used to any extent commercially.

In general, the problems of fluoride scrubbing in a normal superphosphate plant are quite similar to those encountered in a wet process phosphoric acid plant. Scrubbing liquors represent the only aqueous waste stream from most normal superphosphate plants, except for spill cleanup. Solid spills are usually recovered if possible. Liquid spills are washed to a sump for collection and sent to the gypsum pond if a pond is available.

Triple Superphosphate Production

Gaseous fluorides are evolved in the production of triple superphosphate. Fluoride evolution is more constant than in normal superphosphate production and varies between 32-40% of the fluoride in the rock. For a 3.5% fluoride rock this corresponds to a fluoride evolution of 10-12 pounds per ton of product. In run-of-pile triple superphosphate production fluoride is evolved principally in the mixer and conveyor belt (or den) with a minor amount evolved in the storage area. Slack(20) reports the fluoride distribution for ROP triple superphosphate production to be as follows:

Fluoride Disposition	% Total Fluorine Initially in Rock
Evolved at mixer, belt and transfer conveyors	31.4-33.3
Evolved in storage	2.0-2.8
Retained in product	63.9-66.6

In addition, when the triple superphosphate is granulated after curing, scrubbing of the fumes from the dryer may be required as small amounts of fluoride may be evolved.

When granular triple superphosphate is made directly from rock and phosphoric acid, fluoride evolution occurs principally in the reactor, mixer, dryer, cooler, and screens; the total offgas must be scrubbed for fluoride removal.

Almost all triple superphosphate plants are operated in conjunction with a wet process phosphoric acid plant. Therefore, unless the fluoride is to be recovered for sale, the scrubber solution is principally pond water plus some fresh water, both of which are returned to the acid plant gypsum ponds after use. Scrubber operation is similar to that encountered in normal superphosphate production, and the waste stream compositions are similar. Fluoride added to the gypsum pond will amount to about 10-12 pounds per ton of product. Fluoride can be recovered for sale by using a dilute fluosilicic acid scrub solution, as in normal superphosphate production, if economics justify the recovery.

Ammonium Phosphate Production

In the preparation of ammonium phosphate substantial quantities of ammonia are volatilized from the neutralizer and granulator. Process economics require that the ammonia be recovered. This is normally done by scrubbing the gas stream from the neutralizer-granulator with phosphoric acid. The phosphoric acid scrub combines with the incoming process acid which feeds the neutralizer. A portion of the mixed acid stream recycles back to the scrubber. Scrubbing removes most of the ammonia from the gas stream. However, the phosphoric acid scrub solution contains 1-3% fluoride, and optimum scrubber operation for ammonia recovery results in the stripping of some of the fluoride from the acid. The result is a gas stream containing substantial amounts of fluoride and a small amount of ammonia. The fluoride volatilized ranges from 0.1 to 0.3 pounds per ton of product.

Air pollution control regulations usually require that the fluoride be scrubbed from the gas stream. Scrubbing is usually accomplished with water. The scrubber flow required varies from 500-3000 gallons per ton of product; the fluoride concentration in the exit scrub water ranges from 25-250 mg/l. The ammonia concentration in the scrub water varies from 5-50 mg/l. Scrub solution can be recycled with a resulting increase in contaminant concentrations.

When the ammonium phosphate plant is operated in conjunction with a wet process phosphoric acid plant the waste scrub solution can be discharged to the gypsum pond. Pond water can be used as the scrub solution.

Some ammonia is also evolved from the dryer. The gas from the dryer also contains substantial amounts of particulate matter. The solids are removed in a cyclone separator and the gas stream is scrubbed with phosphoric acid to recover the ammonia. The scrubbing can occur in the same unit used to scrub the gas from the neutralizer and granulator or in a separate scrubber. Where a separate scrubber is used, a separate tail gas scrubber for fluoride removal may also be required. The scrub solution from this tail gas scrubber would then be combined with that from the other fluoride scrubber.

Process spills are washed to a sump system with water and returned to the process if possible. Otherwise they are normally transferred to a holding pond and then discharged. If a gypsum pond is available the wash solution may discharge to it.

Ammoniated Superphosphate Production

In the production of granular ammoniated superphosphate ammonia and dust particles are evolved from the ammoniator-granulator and dryer. The dust is removed from the gas stream with cyclones. The ammonia is then removed by scrubbing the gas with recycled water. To control the ammonia concentration in the recycled scrub water at the required level a portion of the scrub is bled off and returned to the process. The bleed is usually mixed with the ammoniating solution or returned directly to the ammoniator. When the scrub is not recycled to the process the scrub solution may be used on a once-through basis. The ammonia concentration is quite low and the solution is discharged to a holding pond or receiving waters. Gypsum pond water can be used as the scrubbing medium when available.

When spills occur they are usually washed to a sump system with a minimum of water. The preferred practice is to recycle the material from the sump to the process. However, in some plants the material is discharged to a pond or receiving water. The composition of the wash solution is difficult to predict but usually contains substantial amounts of ammonia and phosphate.

Granular NPK fertilizers can be produced in equipment similar to the equipment used for ammoniated superphosphate production. Waste stream problems are similar to those encountered in ammoniated superphosphate production. Waste streams generated from process spills are more complex since they may contain potassium, chloride, sulfate, nitrate, and urea in addition to ammonia and phosphate.

Potash Production

The production of potassium chloride by flotation beneficiation generates three waste streams: a clay slimes waste, a solid sodium chloride waste, and a brine bleed for impurity control. The sylvinite ore may contain up to 1.5% insoluble clay materials. The clay is separated fm the NaCl-KCl mixtures as a slime. The slime is washed to remove KCl, dewatered, and discharged to a tailing dump. On a dry weight basis, the clay slimes accumulate at the rate of 30-80 pounds per ton of KCl product depending on the clay content of the ore.

In some cases the sodium chloride from the process may be sold. Normally, however, the sodium chloride is dewatered to recover the KCl-containing brine and then discharged to the tailings dump. Transfer of the NaCl to the dump is usually as a saturated water slurry. The NaCl discharged can amount to as much as 1.5 tons per ton of KCl product depending on the NaCl-KCl ratio in the sylvinite ore. In some plants the clay slimes and sodium chloride waste are combined and sent to a single tailings dump.

In order to control the level of impurities in the recycle brine solution it is necessary to bleed off a portion of the brine from the system on a continuous basis. The discarded brine is saturated with sodium chloride and potassium chloride. It will also contain lesser amounts of magnesium, calcium, and sulfate, as well as small amounts of organic materials which are added to the brine in the flotation circuit. It is the presence of the magnesium, calcium, and sulfate which makes the bleed necessary. The bleed volume is held to a minimum to reduce the KCl loss. The volume of bleed required depends on the concentration of the critical impurities in the sylvinite ore, and can range as high as 100 gallons per ton of product.

In the production of potassium chloride from sylvinite ore by solution-recrystallization the same three waste streams are produced. The only difference is that the brine bleed for the solution-recrystallization process will not contain the organics used in the flotation process.

In the production of potassium chloride from brines at Bonneville and Searles Lake any aqueous waste streams generated are not a problem. They are simply returned to the brine source.

Liquid and Bulk Blend Fertilizers

In the normal operation of liquid fertilizer and bulk blend fertilizer plants no aqueous waste streams are generated by the processes themselves. The wastes from these plants are generated either by process spills or by washdown of equipment. Where possible, solid spills are collected and returned to the mixing equipment. Liquid spills are washed, usually with water, to a sump system. Contaminated water from equipment washdown is also sent to a sump system. It is impossible to define the composition of the aqueous wastes collected in the sump. However, it will normally contain ammonia, potassium, nitrate, chloride and phosphate, and possibly sulfate and urea. The volume of waste generated is equally difficult to define since it will depend on the frequency of equipment washdown required and on the care used in controlling process spills.

ENVIRONMENTAL EFFECTS OF AQUEOUS EFFLUENTS

EFFECTS OF AQUEOUS EFFLUENTS ON RECEIVING WATERS

Aqueous effluents from fertilizer plants which discharge into receiving waters can have three basic effects on the water environment. They can affect:

- aesthetic or recreational value of the receiving water
- renovation or reuse of the receiving water
- biological and physiological changes in organisms in the receiving water or those using the water.

In most cases these effects are interrelated. Wastes which reduce the aesthetic or recreational value of water can also affect water organisms and water reuse.

It is impossible to define quantitatively the aesthetic value of a particular water environment. However, it is easy to recognize the effect of uncontrolled waste discharge on such an environment. Floating material, oil slicks, scum, turbidity, color, odor, excessive plant growth, all serve to detract from the beauty of the water source. The ultimate aesthetic value of a water environment will depend on the value which mankind places on maintaining the environment in a clean and natural state.

There is an increasing awareness in the United States of the need to maintain an adequate supply of water for recreational purposes. This has resulted in initiation of long-range planning to supply these recreational needs. The National Technical Advisory Committee on Water Quality Criteria(34) has made the following recommendation with regard to recreation water used in secondary contact recreation activities:

> "Surface waters should be suitable for use in secondary contact recreation--activities not involving significant risks of ingestion--without reference to official designation of recreation as a water use. For this purpose, in addition to aesthetic criteria, surface waters should be maintained in a condition to minimize potential health hazards by utilizing fecal coliform bacteria.
>
> Surface waters, with specific and limited exceptions, should be of such quality as to provide for the enjoyment of recreational activities based upon the utilization of fishes, waterfowl, and other forms of life, without reference to official designation of use.

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The overall objectives of the committee's recommendations are to insure that water quality management programs for recreation will include criteria to:

1. Provide for and enhance general recreational use of surface waters.
2. Enhance recreation value of waters designated for recreation use.
3. Provide special protection for the recreation user where significant body contact with water is involved.

If these criteria are to be met careful control must be maintained over waste waters discharged into recreational waters.

Waste streams discharged into receiving waters can have a significant affect on the subsequent use or renovation of the water. Dissolved organics, dissolved inorganics, and toxic materials can seriously interfere with subsequent utilization of receiving waters for public water supplies, animal life, and irrigation. Dissolved materials can cause corrosion problems, scaling and undesired side reactions in waters used for industrial purposes, and require expensive water purification prior to use.

Industrial water quality criteria vary over wide ranges. Some industries can get by with very poor quality water, while others, such as the brewing industry, require high quality water. In general, any waste water dumped into receiving waters will impair the usefulness of the water to subsequent industrial users.

The same general statement can be made with regard to the effects of waste water on aquatic organisms. Any pollutants added to the receiving water can change the natural environmental conditions of the water and affect aquatic organisms. If these changes are excessive, serious damage to the organisms may result. To minimize these effects careful control must be maintained over waste waters discharged to the environment.

PARAMETERS FOR EVALUATING AQUEOUS EFFLUENTS

There are a number of factors which must be considered in evaluating the effects of aqueous effluents from fertilizer plants which discharge to the environment. These include the normal or conventional pollution parameters such as pH, BOD, temperature, etc. In addition, there are a number of other contaminants, principally inorganic ions, which must also be considered on an individual basis. These include plant nutrients such as ammonia and phosphate, and potentially toxic materials such as fluoride and elemental phosphorus. A list of the major factors to be considered in evaluating fertilizer plant aqueous effluents is given below. Each of these factors and its effect on the receiving waters is discussed in the following sections.

Conventional Pollution Parameters

pH - Alkalinity - Acidity

Biochemical Oxygen Demand (BOD)

Chemical Oxygen Demand (COD)

Total Oxygen Demand (TOD)

Total Organic Carbon (TOC)

Dissolved Oxygen (DO)

Dissolved Solids

Turbidity

Color

Temperature

Coliform

Major Inorganic Contaminants

Phosphate

Ammonia

Nitrate

Fluoride

Potassium

Sulfate

Chloride

Phosphorus

Suspended Solids

Minor Inorganic Contaminants

Chromates

Heavy Metals

Principal Organic Contaminants

Urea

Monoethanolamine

Lubricating Oils

The limits set by the regulatory agencies on various contaminants and pollution indicators in receiving waters vary significantly depending on the anticipated use of the receiving waters. They also vary from state to state. It is impossible, therefore to define a standard limit for the various parameters which is applicable to all areas of the United States. Typical of the water quality standards used are those of the State of Florida which are presented in part in Table 14.

Conventional Pollution Parameters

The pH of an aqueous solution is defined as the negative logarithm of the hydrogen ion concentration. The pH scale ranges from 0 to 14 and a pH of seven represents a neutral solution. When the pH value is less than seven a solution is acidic, while a pH value greater than seven indicate an alkaline solution. Most natural fresh waters have a pH close to eight and aquatic life, both animal and plant, exists most effectively in water that is near this value. Most aquatic life can tolerate a pH range from 5-9 without serious consequences. If the pH value of a water environment is outside this range for more than brief periods, the mortality rate of most aquatic life will be high. Therefore, care must be taken to control the pH of waste streams discharged to the environment. Most state water quality standards set the pH range for fresh water systems between pH 6.5 and pH 8.5.

The pH is an indication of, but not a measure of, the alkaline or acidic materials present in a water environment. Acidity and alkalinity are reciprocal terms. Total acidity is defined as the amount of standard base required to bring a water sample to pH 8.3. Total alkalinity is the amount of acid

TABLE 14

TYPICAL LIMITS FOR CONVENTIONAL POLLUTION PARAMETERS

The following general water quality standards were set by the Florida Air and Water Pollution Control Commission.

> 28-5.05 Water quality standards; specifies. -
>
> (1) The criteria of water quality hereinafter provided will be applied only after reasonable opportunity for mixture of wastes with receiving waters has been afforded; the reasonableness of the opportunity for mixture of wastes and receiving waters shall be determined on the basis of the physical characteristics of the receiving waters and the methods in which the discharge is physically made shall be approved by the regulatory agency.
>
> (2) The following water quality standards shall be the criteria for pollution when concentrations exceed following limitations:
>
> pH - of receiving waters shall not be caused to vary more than one (1.0) unit above or below normal pH of the waters; and lower value shall be not less than six (6.0), and upper value not more than eight and one-half (8.5).
>
> Dissolved Oxygen - shall not be artificially depressed below the values of four (4.0) ppm.
>
> BOD - shall not be altered to exceed values which would cause dissolved oxygen to be depressed below the limit listed above and, in no case, shall it be great enough to produce nuisance conditions.
>
> Dissolved Solids - not to exceed five hundred (500) mg per liter as a monthly average or exceed one thousand (1000) mg per liter at any time.
>
> Turbidity - shall not exceed fifty (50) Jackson units as related to standard candle turbidimeter above background.

TABLE 14 (Continued)

Temperature - shall not be increased so as to cause any damage or harm to the aquatic life or vegetation of the receiving waters or interfere with any beneficial use assigned to such waters.

Oils and Greases - shall not exceed fifteen (15) mg/l, or that no visible oil, defined as iridescence, be present to cause taste and odors, or interfere with other beneficial uses.

Detergents - shall not exceed one-half (0.5) mg/l.

Fluorides - for waters not used for public water supplies, shall not exceed 10.0 mg/l as fluoride ion or will not interfere with other beneficial uses.

Chlorides - chlorides shall not exceed two hundred fifty (250) mg/l in streams considered to be fresh water streams; in other waters of brackish or saline nature the chloride content shall not be increased more than ten per cent (10%) above normal background chloride content.

Chromium - shall not exceed 0.50 mg/l hexavalent or 1.0 mg/l total chromium in effluent discharge and shall not exceed 0.05 mg/l after reasonable mixing in the receiving stream.

*Abstracted from the rules of the Florida Air and Water Pollution Commission Chapter 28-5, Supplement #62.

required to bring a water sample to pH 4.5. Thus, a water sample can be both alkaline and acidic at the same time. Strong acids are toxic if they drop the pH below 6.0 but do not appear to be toxic above a pH of 6.0. Strong bases do not appear to be toxic below pH 9.0. Weak acids can be toxic at a pH value considerably above pH 6.0 because of the anion or the compound itself; weak bases can be toxic at pH values below 9.0 due to the cation or unionized molecule. The additions of any materials which lowers the pH below 6.0 or above 9.0 can be harmful to aquatic life.

Biochemical oxygen demand (BOD) is defined as the oxygen required for oxidation of soluble organic matter by bacterial action in the presence of oxygen. As such it is a measure of the biodegradable organics present in a waste stream. If the biochemical oxygen demand of a waste stream raises the BOD of the receiving water excessively it can result in the reduction of the dissolved oxygen in receiving water to a point where aquatic life suffers deleterious effects. A high BOD can be an indication of the presence of toxic organic materials in a waste stream. However, it is generally necessary to know the particular organics present to determine the toxic effects of a given waste stream.

Chemical oxygen demand (COD) is defined as the oxygen required to chemically oxidize the organic compounds present in a waste water stream. The COD is a measure of most, but not all, of the organic compounds which may be dissolved in a waste stream. It is an important parameter since it measures the nonbiodegradable organics in the waste water as well as those which are biodegradable. A high COD for a waste stream can result in a reduction in the dissolved oxygen in the receiving water and a resultant deleterious effect on aquatic life. As is the case with BOD, COD is no measure of the toxic affects of specific organic materials.

The total oxygen demand (TOD) of a waste stream is defined as the oxygen required for the oxidation of all carbon, hydrogen, and nitrogen in the waste and partial oxidation of the sulfur compounds in the waste. TOD is a recently developed pollution parameter and has not been widely used. However, it is a valuable tool for evaluating the oxygen requirements for a given waste stream. As is the case with BOD and COD, a high TOD in a waste stream indicates the strong possibility of a decrease in dissolved oxygen in the receiving water and subsequent damage to aquatic life.

Total organic carbon (TOC) is a measure of all the organic materials present in a waste water stream. In combination with COD and BOD it is the best measure of the nonbiodegradable organic materials in the waste. The TOC measurement is a relatively new one and quantitative TOC data for most waste streams is limited. A high TOC indicates high potential for low dissolved oxygen.

Oxygen is required to sustain aquatic life. The dissolved oxygen content of a waste stream or receiving waters is, therefore, an important parameter in determining the pollutional effects of the particular water source. The solubility of oxygen in water is temperature dependent and ranges from 11.3 mg/l at 10 °C to 5.6 mg/l at 50 °C. In warm waters, fresh water organisms require a continuous dissolved oxygen content of at least 5 mg/l to sustain good growth.(34) In cold water, fresh water organisms require a higher dissolved oxygen (>6 mg/l) for good growth. Salt water organisms apparently can exist for long periods of time on a lower dissolved oxygen than is possible with fresh water life. As a general rule, any time the dissolved oxygen drops below 4 mg/l for any period of time all aquatic life will be adversely affected.

Total dissolved solids, as the name implies, is a measure of the solid material dissolved in a water sample. It does not include, however, soluble materials such as vegetable oils, animal oils, and petroleum oils which are volatile or extractable with organic solvents. It is, therefore, essentially a measure of the dissolved inorganic materials in a water sample, principally mineral salts. High dissolved solids in a waste stream can have several effects on the receiving waters. They can impart a mineral taste to drinking water and possibly produce physiological effects in humans and animals. High mineral salt concentrations in drinking water have resulted in gastrointestinal symptoms, wasting disease, and sometimes death in livestock. The United States Public Health Service set a limit of 500 mg/l dissolved solids in public water supplies. The dissolved solids may contain materials which are toxic at very low concentrations. These toxic materials must be determined by additional tests, and the limits for public water supplies are set for specific materials. The 500 mg/l dissolved solids limit assumes the individual dissolved solids are relatively nontoxic and are harmful only at high concentrations where their osmotic effect in organisms becomes excessive.

High dissolved solids can cause corrosion of metals and materials of construction. They can cause scaling problems in cooling water systems, and can make more frequent blowdowns necessary in cooling water and steam generation systems which recycle their water.

Turbidity is a measure of the suspended material in water, and is determined by the opacity or light scattering caused by the suspended matter. Turbidity in a waste stream can have a number of harmful effects on the receiving waters. It can have an adverse effect on the aesthetic quality of the water. High turbidity can reduce the light reaching aquatic plant growth thus reducing photosynthesis. Settling of suspended matter can cause damage to stream, river, and lake bottoms which interfere with fish spawning and adversely affect other animal life. Long term exposures to high levels of suspended solids (>100 mg/l) can have a very serious effect on plant and animal life. At 270 mg/l, suspended solids were reported to cause a high percentage of deaths in rainbow trout,(35) and concentrations above 80 mg/l are unlikely to support good fish growth.(36) Suspended solids in irrigation water can cause excessive plugging and wear in irrigation equipment and restrict water flow. Deposits of suspended solids on irrigated land can cause crusting which interferes with seed emergence. Suspended solids in water used for industrial purposes may make filtration or coagulation necessary prior to use.

Color in waste water can have three principal effects on the receiving waters. Color can adversely affect the aesthetic value of the water; reduce the light reaching plant life; and is objectionable in drinking water. Excessive color in water to be used in public water supplies must be such that it can be removed by the water treatment plant. The limit set by the United States Public Health Service is 75 color units. Excessive color can reduce the aesthetic and recreational value of water not only from the color itself but by reducing the water clarity. Photosynthesis by plant life depends on the light reaching the plants. A minimum of 5% of full sunlight is required to maintain the oxygen balance in water by photosynthesis and it is estimated that many plants require at least 25% of full sunlight for maximum photosynthesis.(34) Color in the water can serve to reduce the light reaching the plants at lower depths and thus limit photosynthesis.

Thermal pollution of water sources must be considered a serious problem. High temperature waste waters can raise the temperature of receiving waters with several deleterious effects resulting. Most aquatic organisms require oxygen to maintain life. This requirement is normally supplied by oxygen dissolved in the water. The solubility of oxygen in water decreases with increasing temperature. Therefore, if the water temperature becomes too high the dissolved oxygen may be reduced to the point where growth of aquatic organisms is adversely affected. Chemical and biochemical reactions which occur in water increase in rate when the temperature increases.

Therefore, the oxidizable materials will be reacted in a shorter stream length at higher temperatures. This can lead to an oxygen depletion in the water which could adversely affect the growth of aquatic organisms. All aquatic organisms grow best within specific temperature ranges. Any changes in temperature which exceed the optimum range can adversely affect organism growth. The optimum temperatures can vary widely for the many different aquatic species of plant and animal life. Table 15 shows the maximum and minimum temperatures for several varieties of fish acclimated to specific temperatures.(37,38)

The optimum temperature ranges for aquatic plants vary depending on the species. For instance, different algae species grow best at different temperatures. Blue-green algae grow best at 35-40 °C, green algae at 30-35 °C, and diatoms at 18-20 °C.(39) Long term changes in water temperature can lead to changes in the predominant algae species in a water environment.

TABLE 15

TEMPERATURE RANGE FOR FRESHWATER FISHES(37,38)

Species	Maximum*		Acclimated to	Minimum*	
	°C	Hrs	°C	°C	Hrs
Large mouth bass	32	72	20	5	24
Bluegill	31	60	15	3	24
Channel catfish	30	24	15	0	24
	34	24	25	6	24
Brook trout	23	133	3	-	--
	25	133	20	-	--

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*Values are LD_{50} temperature tolerance limit. 50% of fish survived water temperature.

Coliform bacteria are the recommended indicator of the presence of fecal matter in water. Fecal coliform organisms in water are indications of recent fecal pollution. Nonfecal coliform organisms may be due to less recent fecal pollution, soil runoff water, or fecal pollution containing only those organisms. Water containing human or animal waste is dangerous because of the possible presence of pathogenic microorganisms. These include members of the salmonella and shigella genera, vibrio coruma, endamoeba histolytica, and enteric viruses.(40) Coliforms, although they come from the same source as the pathogens, serve as harmless indicators. In general, the presence of coliforms is an indication of possibly dangerous pollution. As long as sanitary waste is kept separate from other fertilizer plant waste streams, it does not represent a major problem to the fertilizer industry. Such streams are treated in the same manner as any other sanitary waste.

Inorganic Contaminants

Inorganic materials are the principal contaminants found in fertilizer plant waste waters, and represent the major water pollution problems facing the fertilizer industry today. The rapid increase in production of ammonia and ammonia-based fertilizers has resulted in the generation of large volumes of aqueous wastes contaminated with ammonia. The technology required for reducing the ammonia in the waste to the desired levels is not well developed and the processes that are available are costly.

Ammonia in waste water can have a number of deleterious effects when discharged to the receiving water:(41)

1. Ammonia can contribute to rapid algae growth which can ultimately lead to eutrophication.
2. Ammonia can be toxic to fish.
3. Ammonia can restrict waste water renovation and reuse.
4. Ammonia can have a detrimental effect on the disinfection of water supplies.
5. Ammonia can be corrosive to some metals and materials of construction.
6. Ammonia can have a detrimental effect on water odor and taste.
7. Ammonia can exert an oxygen demand.

Ammonia is a nutrient for plant growth. Considerable experimental evidence shows that nitrogen, as ammonia, can contribute greatly to the rapid growth of algae. In general, ammoniacal nitrogen is assimilated more rapidly by plant life than any other form of nitrogen.(41,42) Very rapid algae growth due to an excess of nutrients can lead to eutrophication. Considerable controversy exists among reputable scientists as to the role of nitrogen (and ammonia) in the problem of eutrophication. Until the controversy over the cause(s) of eutrophication is resolved, nitrogen in waste water in any form, and particularly as ammonia, should be considered as a likely cause of eutrophication and treated accordingly.

Ammonia in water can be toxic to fish. Lethal ammonia exposures for various species are reported to vary from 0.2-5.0 mg/l.(43) The toxicity is dependent primarily on nonionic ammonia and unassociated ammonium hydroxide. Therefore, pH has an important effect on ammonia toxicity.(44) Field tests show that when the pH is 8 or above the ammonia content as nitrogen should not exceed 1.5 mg/l.(34) At levels above 1 mg/l ammonia inhibits the ability of hemoglobin to combine with oxygen and fish may suffocate.(34,44)

When water is disinfected with chlorine any ammonia present in the water will react with the chlorine to form chloroamines. The chloroamines are bactericidal but are slower acting and less effective than chlorine.(45) Chloroamine concentrations as low as 0.4 mg/l are reported to be toxic to fish.(46)

Ammonia water can be quite corrosive to certain metals. Copper and zinc alloys are rapidly attacked even at low ammonia concentrations.(47,48) Ammonium salts also attack concrete made from Portland cement.(43)

Most states do not at present have a specific water quality standard for ammonia. For those states which do have ammonia standards, they vary from 0.02 to 3.5 mg/l as nitrogen.(41) In states without ammonia standards ammonia can be included, by implication, in those standards for toxic substances.

Phosphorus in the oxidized state is a plant nutrient and essential for all forms of plant growth. When other conditions are favorable, additions of low phosphate concentrations to an aqueous system can lead to rapid growth of algae and other vegetation. Many experts consider phosphorus and nitrogen to be the principal causes of excessive aquatic plant growth which leads to eutrophication. The available phosphorus required for algae growth is reported to be quite low. Concentrations ranging from 0.01-0.05 mg/l are reported to be sufficient for growth.(34) Available phosphorus is dependent on the total phosphorus concentration.

Phosphorus in the oxidized state is not normally considered toxic to animal life. As long as the phosphate concentration is less than 100 mg/l,its presence in public water supplies is not considered a problem. Phosphates can cause scaling problems in water used for steam generation and cooling purposes. At concentration greater than 0.5 mg/l they interfere with normal coagulation and settling processes in water purification plants.(34)

Elemental phosphorus must be considered quite toxic to animal life. Elemental phosphorus dissolves in water only to the extent of 3 mg/l. However, when water contacts phosphorus, colloidal phosphorus particles may be formed which raise the phosphorus concentration drastically. The lethal dose for elemental phosphorus in humans is reported to be 100 mg and the chronic dose is 1 mg/day.(49) In-take of elemental phosphorus causes bone and liver damage and a chronic poisoning resulting in progressive weakness and anemia.(50,51) Elemental phosphorus concentrations as low as 0.05 mg/l were reported to be toxic to fish when the exposure time was 163 hours.(52)

Elemental phosphorus in waste waters represents a potential fire hazard. Evaporation of waste water containing colloidal phosphorus particles can allow the phosphorus particles to become dry. Oxidation of the dry particles can result in a fire if additional combustible materials are present.

Nitrate ion is a nutrient for aquatic plant growth, and as such can be considered a potential cause of eutrophication. Assimilation of nitrate by plants is, in general, less rapid than the uptake of ammonia. Nitrate ion can be toxic to humans and ruminants. It is reported to cause methomoglobinemia (nitrate cyanosis) in babies if the nitrate concentration in water exceed 70 mg/l.(51,53) The United States Public Health Service sets the maximum nitrate content for drinking water at 45 mg/l. Nitrates are also reported to cause methemoglobinemia in cattle and pigs. However, fairly high concentrations (>1000 mg/l) are required.(34)

Soluble fluorides present in waste water must be considered to be toxic to animal and plant life. Fluorides in drinking water can cause serious problems. Continuous ingestion of water containing 2-3 mg/l of fluoride is reported to cause mottled teeth, and greater concentration can cause severe fluorosis and even death.(51) Deaths have been reported from the continuous use of water containing 13 mg/l fluoride.(54) The United States Public Health Service has set the maximum limit for fluoride in drinking water at 1.7 mg/l. Fluoride concentration greater than 1.5 mg/l are reported to be toxic to fish,(34) although other studies indicate concentrations of 50 mg/l only stunt growth and reduce reproduction.(20) There is some evidence that fluorides can accumulate in certain organisms which makes potential fluoride poisoning of animal life more likely. Aquatic plant life do not appear to be adversely affected by concentrations of soluble fluorides of less than 50 ppm. Control authorities of the State of Florida report that at pH values above 6.0 a total fluoride content up to 20 mg/l is not harmful for water not used for human consumption, and Florida water quality regulations set a limit of 10 mg/l fluoride in water not used to supply drinking water requirements.(20)

Potassium is not considered to be especially toxic to animal life. As long as the concentration in drinking water does not exceed the limit for total dissolved solids (500 mg/l) potassium should not be a hazard to human life. The United States Public Health Service has not set a limit for potassium in drinking water. Potassium is a nutrient required for plants. As such, potassium in waste waters can serve to accelerate plant growth. If potassium is limited in a given aquatic environment, then potassium added to the system through waste water could possibly result in excessive and objectionable plant growth.

Sulfate ion in water in limited amounts (<500 mg/l) is not considered hazardous to animal life. High concentrations in drinking water can have a laxative effect on humans,(55) and high concentrations (2104 mg/l) are reported to cause a progressive weakening and death of cattle.(56) The United States Public Health Service has set a limit for sulfate in drinking water of 250 mg/l. Sulfur is a secondary nutrient required for plant growth. Therefore, sulfate ion in waste water serves as a nutrient for aquatic plant growth. Sulfate ion in water used for cooling purposes or steam generation can be a potential cause of scale. Normally, however, the sulfate concentration must be quite high to be a problem. High sulfate in boiler or cooling water which is recycled causes more frequent blowdown and a larger blowdown waste stream.

Chloride in waste water is not a particular problem if the concentration does not exceed 500 mg/l. The United States Public Health Service has set the chloride limit for drinking water at 250 mg/l. The principal objection to chloride in drinking water is the effect on taste. Chloride concentrations of greater than 5000 mg/l have been reported to be toxic to certain types of bird life.(34) The effect of chloride on plant life is difficult to evaluate. Many aquatic plants can adjust to wide ranges in chloride concentration. Some plants are, however, susceptible to chloride damage and concentrations as low as 100 mg/l in irrigation water can be harmful to certain citrus and fruit.(57) Chloride in boiler and cooling water contributes to the dissolved solids. When the water is recycled, high chloride concentrations lead to more frequent blowdown and a larger blowdown waste stream. High chloride concentrations can also lead to increased corrosion of metal surfaces.

Chromium in the hexavalent state ($CrO_4^=$, $Cr_2O_7^=$) must be considered extremely toxic to plant and animal life. The United States Public Health Service sets the limit for hexavalent chromium in public water supplies at 0.05 mg/l. Continuous intake of chromates has been reported to cause intestinal inflammation, kidney damage, and lung cancer.(51) Chromate concentrations greater than 0.2 mg/l are toxic to algae and other aquatic plant life, and higher concentrations (>1 mg/l) are toxic to many species of fish.(34) Marine life, except for mollusks, shows a somewhat greater tolerance to hexavalent chromium than most fresh water life. Mollusks, such as oysters, have a very low tolerance to chromates, and concentrations of 0.01 mg/l are reported to be toxic to oysters.(34)

The heavy metals, as a group, must be considered extremely toxic to plant and animal life. The United States Public Health Service sets the limit for most heavy metals in drinking water at 0.05 mg/l. Some heavy metals are permissible at higher levels (i.e., Zinc - 5.0 mg/l) but still must be considered very toxic. The effect of many heavy metals on plant and animal life is complicated by the fact that their toxicity depends somewhat on the concentration of calcium and magnesium in the water.

Organic Contaminants

Organic contaminants are not a major problem in the aqueous effluents from fertilizer plants. The principal problems are urea from urea plant and blending plant wastes; monoethanolamine in ammonia plant wastes, and oil leaked from pumps and compressors into various waste streams. Some organic compounds are frequently added to cooling water systems for biocidal purposes, but the concentrations are usually quite low and do not represent a major contamination problem.

Urea does not represent a serious pollution problem at the present time, and no specific standards for urea in water supplies have been set by any of the states. Urea is a source of nutrient nitrogen for aquatic plants and can contribute to increased plant growth. However, urea assimilation by plants is relatively slow, and it is doubtful that urea can be considered as contributing significantly to eutrophication. Urea has been reported to be toxic to certain species of fish but only at concentrations of 30,000 mg/l.(58) Urea is used as an animal food supplement so should not be considered as toxic to animal life.

Monoethanolamine (MEA) is a minor pollution problem in the aqueous effluents from ammonia plants. The principal effect of MEA on the waste stream and receiving water is that it adds to the BOD load of the stream. MEA concentrations greater than 1500 mg/l are reported to be toxic to certain species of fish upon long term exposure.

Oils in waste streams can be a serious pollution problem. The deleterious effects of oil in the receiving waters are several. The oil can create an odor and taste problem in public water supplies. It can coat the water with a thin film, thus affecting the aesthetic value of the water. The oil film can interfere with the dissolution of oxygen in the water and with photosynthesis. Direct contact of fish with oil can result in the oil interfering with the respiratory action of the gills. The oil may also taint the flesh of the fish if ingested. Oil can coat plant life, such as algae, and kill it. Suspended solids in the water may be covered with oil and settle to the bottom where they can interfere with plant growth and fish spawning. The oil can coat the plummage of waterfowl, thereby destroying their natural buoyancy and insulation. Oil can also affect egg laying in waterfowl if ingested, and oil coating of eggs can reduce hatching. Components of the oil may be toxic to plant and animal life, and it has been reported that concentrations as low as 0.3 mg/l can be toxic to certain fish species.(34,59)

ANALYSIS OF AQUEOUS EFFLUENTS

Adequate control of fertilizer plant effluents requires careful monitoring and anaylsis of waste streams. When possible, continuous monitoring of waste streams is the preferred approach. However, reliable continuous analytical procedures are not available (or have not been adapted to industrial use) for monitoring most of the contaminants found in fertilizer plant waste streams. The only parameters that are analyzed on a continuous basis in a significant number of plants are pH and conductivity.

The frequency of sampling and extent of analysis of most waste streams is dependent primarily on plant location and existing water quality regulations. Most plant sample waste streams at least once a day, and the principal contaminants are determined on a daily basis. In areas where water quality regulations are less stringent samples are usually taken less frequently, and some plants may sample once a week or less. The method of waste disposal can also influence the monitoring and analysis of waste streams. Companies using deep well injection for waste disposal apparently sample and analyze the waste streams far less extensively than companies which discharge into surface waters. Waste streams which discharge into marine waters are monitored less extensively than waste streams discharging into fresh waters.

Inorganics are the principal contaminants in most fertilizer plant waste streams, and are usually analyzed each time a waste stream is sampled. Organic contaminants are less critical in fertilizer plant wastes, and organic indicators such as BOD and COD are usually determined less frequently.

The analytical methods for measuring the conventional pollution parameters (i.e., pH, turbidity, BOD, etc.) used by the fertilizer industry are well developed, and are described in several references.(60,61,62)

A variety of analytical procedures is available for each of the various inorganic ions found in fertilizer plant waste streams. Most of the methods suitable for analyzing waste water streams to the required minimum concentration levels are described in the "Manual on Industrial Water and Industrial Waste Water" published by the ASTM.(62) Several other good references are also available which describe the required analytical procedures.(60,62,63,64,65)

CONTROL AND TREATMENT OF AQUEOUS EFFLUENTS

This chapter describes the general methods used by the fertilizer industry to control and treat aqueous waste streams. Use of these methods by the various segments of the fertilizer industry is discussed.

CLASSIFICATION OF TREATMENT METHODS

Despite the multitude of fertilizer materials produced by the fertilizer industry, the methods used by the industry to control and treat contaminated aqueous waste streams are relatively limited. These methods can be divided into five general categories:

1. Disposal methods
2. Process improvements and modification
3. Water recycle and reuse
4. Physical treatment methods
5. Chemical treatment methods.

Biological treatment methods, which are widely used in treating other industrial and municipal wastes, are almost unknown in the fertilizer industry. This reflects the fact that the principal contaminants found in fertilizer industry waste waters are primarily inorganic materials.

One other approach used by the fertilizer industry for control and treatment of waste water must be considered. It involves the segregation, or lack thereof, of the various waste water streams within a plant. Normally some attempt is made to effect some segregation. Uncontaminated waste waters are usually kept separate from contaminated streams. Once-through cooling water and rainwater runoff from uncontaminated plant areas are typical examples of uncontaminated effluents which are usually kept separate from other waste streams. Separation of various contaminated waste streams may be practiced depending on the treatment each stream requires prior to discharge. As a typical example, cooling water blowdown, which is high in chromate, may be kept separate from other contaminated waste until the chromate is destroyed.

Disposal Methods

Disposal methods are available which currently permit discharge of untreated or partially treated waste waters. These include dilution, ocean disposal, deep well disposal, and discharge to municipal sewer systems. Under the current water quality standards of most states these disposal methods are widely used. As water quality standards become more restrictive, however, these methods will probably become unacceptable. If effluent standards are developed which base the quantities of contaminants which can be released on a unit of production (i.e., pounds of contaminant discharged per ton of product) then it is a certainty that the disposal methods will be unacceptable.

Disposal of waste water by dilution is based on the concept that dilution of the waste water by the receiving water reduces the contaminants present in the waste water to an acceptable level. The restrictions on this form of disposal are that sufficient receiving water must be available for dilution, and that the intended usage of the receiving water must not be adversely affected. Dilution disposal is often combined with some form of physical treatment such as settling or holding ponds.

Disposal by dilution is widely practiced in many areas of the fertilizer industry. However, as water quality regulations become more restrictive and effluent standards are adopted, particularly on nutrient discharge, this form of disposal will become unacceptable. The many plants which now rely on dilution for disposal of untreated or partially treated waste waters will be forced to develop and install treatment processes.

Ocean disposal finds limited use in the fertilizer industry. It is essentially a variation of disposal by dilution. As such it is becoming less acceptable as control criteria become more stringent.

Deep well disposal is widely used by many industries for disposing of contaminated waste waters. Several plants in the fertilizer industry have reported using deep well disposal. In the process the waste stream is injected under pressure into geological formations far below surface and sub-surface water supplies. The disposal depths can range up to 12,000 feet depending on water tables and underlying strata.(66) In certain cases some form of preliminary treatment may be required before final disposal. This usually involves settling for solids removal and/or oil separation. Care must be taken that deep well disposal does not contaminate surface or sub-surface water supplies.

In a few cases, fertilizer plant wastes are discharged into municipal sewage systems. This practice is usually limited to small plants with small waste loads. Typical examples are small liquid mix plants which may discharge equipment washdown and spill solutions into the local sewage systems. This form of disposal has been only partially successful, and will undoubtedly be less acceptable in the future.

Process Improvement and Modification

The most satisfactory method of controlling aqueous waste streams is to prevent or reduce their formation. This approach can result in improved process economics through better yields, as well as reduced waste treatment costs. There are numerous ways in which such improvements can be effected. Improved operational control and preventive maintenance can reduce leaks and spills which create waste streams as well as loss of valuable materials. Process changes can be made so that spill cleanup solutions can be recycled back to the process. Waste streams created by scrubbing feed or product materials from gaseous effluents can be recycled back to the process. Continuous or extensive monitoring of waste streams can be initiated to help in identifying process malfunctions and leaks. Wherever possible, recovery of potentially valuable by-products from waste streams can substantially reduce waste treatment requirements.

Water Recycle and Reuse

Recycling and reuse of waste water can be a most effective and inexpensive method for controlling industrial waste loads. It is widely practiced in the fertilizer industry. Effective reuse of water reduces the volumes of waste water to be treated, reduces the need for large volumes of fresh water, and allows more freedom from upstream water users. Currently, about 75-80% of the gross water requirements of the fertilizer industry are supplied through recycling and reuse of waste water.

The fertilizer industry requires large volumes of cooling water. Recycling of the cooling water is widely practiced in all segments of the industry. Recycling decreases the quality of the water and requires the use of additives and special materials of construction to control scaling and corrosion. The advantages of cooling water recycle, however, offset these added costs. Once-through cooling water operation is only used when water is readily available and when the cooling water effluent can be discharged without treatment except for temperature reduction. Contaminated water from other plant operations can also be used for cooling purposes to reduce water consumption. As an example, gypsum pond water can be used for cooling purposes in many operations in a phosphoric acid-fertilizer plant complex. Blowdown from the cooling water recycle system represents a small-volume contaminated waste stream. Blowdown can be treated separately from other contaminated wastes, or combined with them to be treated as a single waste stream.

Recycle of steam condensate represents another effective method for water recycle. Normally, boiler operation requires that only condensate which is not contaminated with process materials be recycled. This frequently eliminates the recycling of condensate from such operations as steam stripping. However, condensate not returned to the boiler water can frequently be used to supply other plant water requirements. Boiler water blowdown represents another small-volume source of contaminated waste water. It is often combined with cooling water blowdown for treatment.

Other major consumers of water in the fertilizer industry are the scrubber operations required for treatment of gaseous waste streams. Once-through use of scrubber solution would result in the generation of large volumes of low level waste which would be extremely difficult to treat. By recycling the scrubber solution the waste volume is substantially reduced, and the small-volume, highly contaminated waste stream can be more effectively treated.

Physical Treatment Methods

The physical treatment methods used by the fertilizer industry are relatively few. They are limited primarily to gravity separation techniques and to stripping operations.

Gravity separation methods are used primarily to: remove suspended solids from the untreated waste water; separate solids formed by chemical treatment of the waste water; and to separate any oils present from the waste water. Many of the waste streams generated by the fertilizer industry will contain significant amounts of suspended solids. An obvious example is the gypsum slurry discharged from wet process phosphoric acid plants. Holding or settling ponds are normally used to allow the solids present to agglomerate and settle out. Flocculents are sometimes added to the waste stream to assist settling.

Chemical treatment of waste waters to remove dissolved solids usually generates precipitate which must be removed before the waste water is discharged. Clarifiers, thickness and settling ponds are all used to obtain the required separation. Filtration and centrifugation are rarely used because of the volumes of waste water to be treated and the cost involved.

In some cases the waste water streams may contain significant amounts of oil. Typical examples are process condensate from ammonia plants and cooling water used on pumps and compressors. Oil is a troublesome contaminant in waste waters and should be removed whenever possible. Oils are most easily removed when their concentrations are high; low oil concentrations can be difficult to treat. If the oil is emulsified with the water, its removal is even more difficult since gravity separators are less effective on emulsions. Most plants use API-design oil separators to obtain the required oil removal. Properly operated separators can reduce the oil level in most waste water streams to 25 mg/l or less.(66,67)

Air flotation can also be used for oil removal. In this process, air is dissolved in the waste water under pressure. The air is then released at atmospheric pressure in a tank or basin. Air bubbles, formed by the release of pressure, rise to the surface, gathering oil and suspended solids which can be removed by skimming. Air flotation can reduce oil levels to less than 20 mg/l in most streams, as well as removing substantial amounts of suspended solids.(67)

Stripping can be used to remove volatile species from waste waters. Steam, air, and inert gases are the most commonly used stripping agents. Steam is the preferred stripping agent in most cases since it, plus most volatile contaminants, can be readily condensed to give a concentrated aqueous stream. Air or inert gas stripping of waste waters may simply substitute a gaseous waste problem for a waste water problem. In the fertilizer industry, stripping is limited almost entirely to the removal of ammonia from waste water.

Cooling must be provided to prevent the discharge of warm waters which exceed specified temperature limits. This is usually accomplished through holding or settling ponds which provide sufficient capacity to allow the required cooling to occur before the waste water is discharged. Once-through cooling water is normally treated in this manner. Blowdown from a recycle cooling water system is usually removed from the system at the outlet of the cooling tower or pond and requires no further cooling before discharge. Boiler water blowdown, on the other hand, must normally be cooled before discharge. Cooling is frequently obtained as a result of other treatment processes (i.e., settling ponds for solids removal).

One additional physical treatment method finds some use in the fertilizer industry. In areas of low rainfall and warm climate, solar evaporation can be used to dispose of contaminated waste water. The waste stream is pumped to a holding pond or dump where the water is evaporated and the nonvolatile contaminants collect as a solid residue. This method is especially attractive for fertilizer plant waste which are composed principally of nonvolatile dissolved inorganic materials. Flow to the pond cannot exceed solar evaporation (plus some sub-surface drainage) for extended periods of time without some aqueous discharge from the pond resulting. Normally, water levels in the ponds are maintained substantially below pond capacity to allow for extended periods of high rainfall or low evaporation.

Chemical Treatment Methods

Chemical treatment methods play an important part in the control of fertilizer plant effluents. They are used principally for neutralization of aqueous wastes, precipitation of dissolved inorganics, coagulation of suspended solids and destruction of toxic materials.

Neutralization of strongly basic or acidic waste waters is normally required prior to discharge. In the fertilizer industry, the bulk of the waste waters are acidic or neutral. Where neutralization of acidic waste is required, lime or limestone are the preferred neutralizing agents.

Chemical precipitation can be used to remove certain contaminants from waste waters. Frequently, neutralization and precipitation are combined to effect removal of contaminants. Typical of the combined treatment is the neutralization of acidic gypsum pond water with slaked lime which precipitates both the fluoride and phosphate in the pond water.

Chemical coagulation can be used to assist in the separation of suspended solids and precipitates from waste waters. Coagulation is always followed by some physical treatment to effect separation of the solids from the waste water. Normally, some form of gravity separation is used such as clarifiers or settling ponds.

Waste waters will frequently contain toxic materials which must be destroyed by chemical means. The treatment used will depend on the contaminant under consideration. Typical of such materials is chromate ion which is used for corrosion control in cooling water systems. Blowdown from cooling water systems can contain substantial levels of chromate. The chromate is quite toxic and must be removed from the blowdown stream prior to discharge. Chemical treatment is usually used to destroy the chromate ion since it cannot normally be precipitated as such.

TREATMENT OF NITROGEN FERTILIZER EFFLUENTS

In the production of ammonia, most plants rely on disposal techniques for control of contaminated waste waters. Disposal by dilution or deep well injection are the principal means of handling all contaminated waste waters. Treatment of process waste streams prior to final disposal is usually limited to oil separation and settling. Contaminated cooling water (blowdown) is normally treated for oil separation and chromate destruction before discharge.

Typically, in an ammonia plant the contaminated process waste waters (principally process condensate) flow to oil separators where the oil level is reduced below 30 mg/l. From the separator the waste water flows to a holding pond for settling. Residence time in the holding pond is usually in the range of 10-20 days. On entry to the pond, the waste water is sampled for analysis on a routine basis. From the holding pond the waste water discharges to the receiving waters, and dilution is relied upon to reduce the contaminants to an acceptable level in the receiving water. Some plants may adjust the pH of the waste water prior to discharge.

Cooling water blowdown may be combined with the process waste water or treated separately. Typically, oil is removed from the blowdown using oil separators, and then the chromate is destroyed chemically. Chromate removal can be accomplished by treating the blowdown with sulfur dioxide and lime. The treated blowdown waste stream, containing <0.1 mg/l chromate, then discharges to the holding pond.

Waste water from ammonia plants can be treated for ammonia removal by stripping. However, stripping is practiced in only a few plants. When stripping is used ammonia removal rarely exceeds 60-70%. With high gas flows ammonia removal can be increased to better than 90%. However, such recoveries can only be obtained when the initial ammonia concentrations are high. Reduction of ammonia levels below 30 mg/l using stripping is difficult to achieve. Use of air as the stripping agent can make condensation and recovery of the stripped ammonia a problem. The petrochemical industry makes great use of stripping to remove ammonia from sour water streams(67) where ammonia concentrations are quite high (1000-5000 mg/l). Stripping is of less value in treating ammonia plant waste streams in which the ammonia concentrations are much less.

The current water quality standards for ammonia (or lack thereof) in many localities has resulted in the use of dilution as the principal means of controlling ammonia plant waste waters. As water quality criteria for ammonia becomes more restrictive, dilution will no longer be acceptable as a disposal method (a number of plants are already encountering this situation). Most plants recognize this problem and are centering their development efforts on ways of reducing waste water loads and increasing the recycle of contaminated waste streams. The ultimate objective will be to achieve complete closed loop water reuse. Typical of the methods devised to reduce waste loads is recycling of certain contaminated process condensates back to the process, as now practiced in some plants.

In the production of nitrogen fertilizers such as NH_4NO_3, $(NH_4)_2SO_4$, and urea, the waste water disposal problems are essentially the same as those encountered in ammonia production. The methods of controlling and treating waste water discharges are the same as well. At the present time, most waste streams are disposed of by dilution or deep well injection with little or no treatment prior to final disposal. Any treatment of process effluents prior to discharge usually consists of pH adjustment and settling in holding ponds. Oil separation and chromate destruction is usually provided for cooling water blowdown as well.

Producers of nitrogen fertilizers recognize that disposal by dilution is becoming less aceptable. Possible methods for reducing waste loads, increasing the recycle of contaminated waste water and obtaining completely closed loop water reuse are being extensively studied. Methods for removing contaminants from the waste water to facilitate discharge are receiving less attention.

TREATMENT OF PHOSPHATE INDUSTRY EFFLUENTS

In the phosphate fertilizer industry the treatment and control of aqueous waste waters is greatly affected by the availability of a gypsum pond. In wet process phosphoric acid plants and phosphate fertilizer complexes the gypsum pond serves as a reservoir for contaminated waste. It is standard practice to discharge all contaminated waste waters to the pond. The settled supernate from the pond serves as the source for most plant water requirements including cooling. In some plants, recycled pond water accounts for up to 90% of the gross water requirements. Overflow from the gypsum pond is normally the only contaminated waste stream to be treated prior to discharge. Uncontaminated waste waters such as once-through cooling water and rainfall runoff from uncontaminated plant areas are kept segregated from the pond water system and discharged without treatment. Plants using recycle cooling water systems separate from the pond water system frequently discharge the blowdown stream to the gypsum pond after chemical treatment for chromate removal. When a gypsum pond is not available the phosphate fertilizer plant must provide other treatment facilities for processing the various contaminated waste water streams.

As described earlier, waste water discharged from a phosphoric acid plant gypsum pond contains substantial amounts of fluoride and phosphate. The discharge must be treated to reduce these contaminants to an acceptable level before it is released to the ground waters. In almost every case the treatment procedure used consists of lime neutralization and settling. In most cases double liming and possibly triple liming is required to obtain the desired impurity removal. A typical flowsheet for the double liming of pond water discharge is shown in Figure 29. In this process, slaked lime or a slaked lime slurry is mixed with pond water in a mixing tank. The resulting slurry passes to an agitated settling tank or clarifier. Clear supernate from the clarifier passes to a second mixing tank where additional slaked lime is added. Underflow from the first clarifier is returned to the gypsum pond. The slurry from the second mixing tank flows to a second clarifier. Clear supernate from the second clarifier is discharged to the ground water or is returned to the plant processes as clean water. Underflow returns to the gypsum pond.

Limestone can be used in the first stage of neutralization, but slaked lime is much preferred. Normally, fresh water is used to slake the lime.

With good agitation in the mixers, slurry residence time in each is less than one hour, and in most plants a residence time of 10-15 minutes is normally used. Settling times in the clarifiers are much longer and can run to several hours.

In the first stage of neutralization using slaked lime, the pH of the solution is raised to about 3.6-3.8. Most of the fluoride present in the pond water precipitates, probably as calcium fluoride. The soluble fluoride content of the supernate leaving the first clarifier is in the range of 40-60 mg/l.(69) The phosphate content of the supernate is only slightly reduced (5-10%) in the first neutralization stage. In the second stage of neutralization the pH is raised to 6-7. Almost all of the phosphate and most of the remaining fluoride precipitates. The fluoride probably precipitates as fluorapatite. The supernate from the second clarifier contains 5-20 mg/l fluoride and 10-30 mg/l phosphate. Calcium and sulfate concentrations are reduced somewhat from their original pond water values, but not to the same level as the fluoride and phosphate.

Under water quality standards currently existing in most states, the water from the second stage of liming can be discharged to receiving water assuming some dilution is possible. If either fluoride or phosphate criteria become more restrictive, it is doubtful if lime neutralization can provide the necessary fluoride and/or phosphate removal. Elimination of pond water discharge through increased water recycle, or an improved treatment method for fluoride and phosphate removal, will then be required.

In some localities, water evaporation and sub-surface drainage from the gypsum pond eliminate the need for controlled discharge of a waste water stream from the pond. In such cases

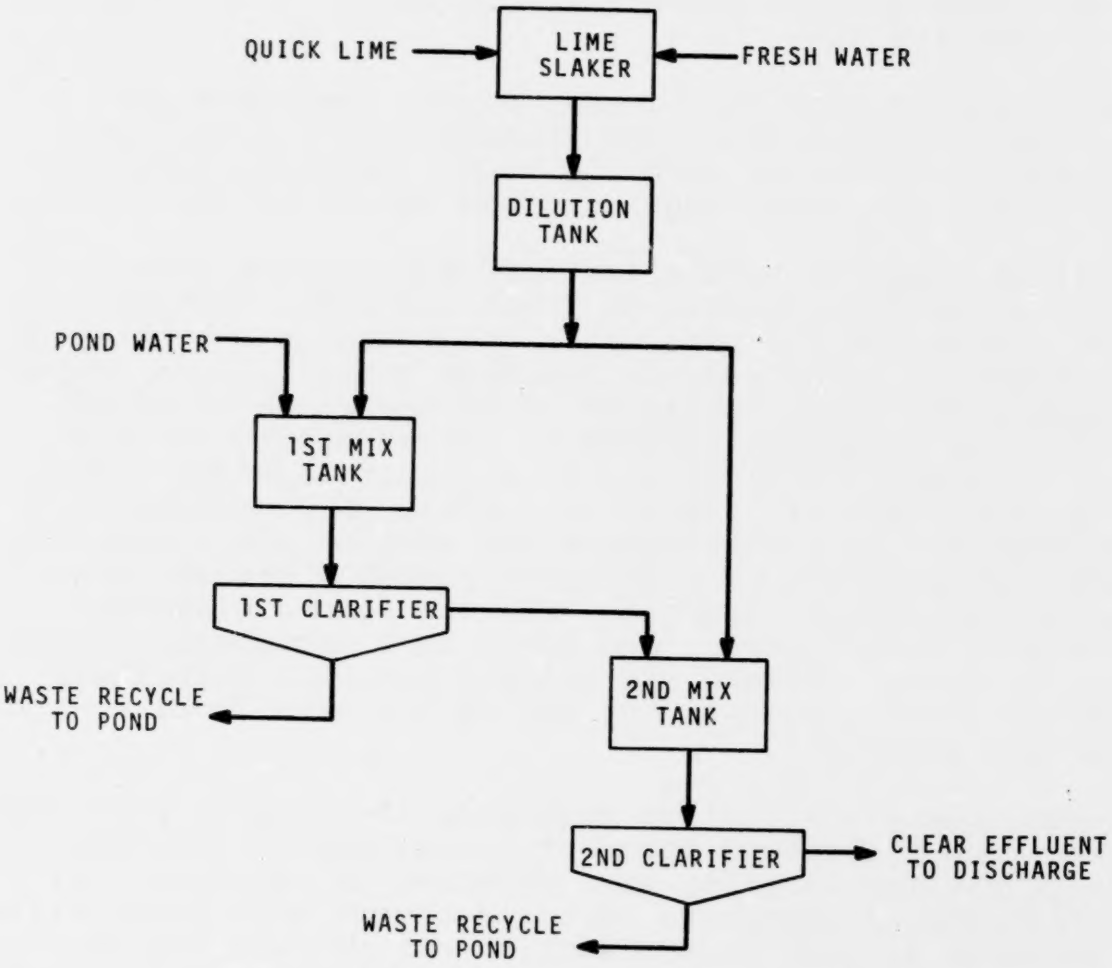
QUICK LIME
LIME SLAKER
FRESH WATER
DILUTION TANK
POND WATER
1ST MIX TANK
1ST CLARIFIER
WASTE RECYCLE TO POND
2ND MIX TANK
2ND CLARIFIER
CLEAR EFFLUENT TO DISCHARGE
WASTE RECYCLE TO POND

FIGURE 29 FLOWSHEET FOR LIME NEUTRALIZATION OF GYPSUM POND WATER (20)

the pond serves as a reservoir where plant waste waters are disposed of without additional treatment. However, as air and water pollution control regulations become more restrictive this technique may not be acceptable and new treating methods will have to be developed.

As described earlier, fluoride-containing scrubber solutions can be a major source of contaminated waste water in any phosphate fertilizer or phosphoric acid plant. Treatment of some form is almost always required for fluoride removal before the waste water can be discharged to the ground water. The ideal solution is to operate the scrubber system in such a way that the fluoride can be recovered for sale as hydrofluoric and fluosilicic acid, metal fluosilicates or metal fluoride. A number of scrubber systems have been designed to permit fluoride recovery.(30,31)

When fluoride recovery is not economical or practical, some form of waste water treatment is required. When a gypsum pond is available, the fluoride scrub solutions can be discharged to the pond where they become a part of the overall pond water system. When a gypsum pond is not available another method of disposal is required. In most cases, this involves lime neutralization of the scrubber solution followed by collection of the precipitated fluoride. To reduce the waste volume to be treated, the scrub solution is recycled and only the bleedstream used to control the fluoride concentration is treated. By neutralizing to pH 7 with slaked lime, the fluoride concentration of the clear effluent will be reduced to 20-30 mg/l after settling.

Waste streams generated by spill cleanup and equipment washdown can be combined with the scrubber solution and treated as a single waste stream. When this is done lime neutralization will remove any phosphate in the waste stream as well as fluoride.

The TVA has developed a process for treating scrubber solutions for fluoride removal using granulated furnace slag. In this process the scrub solution, containing 700 mg/l of fluoride, flows to a settling pond at the slag pile at the rate of 400 gpm. After settling, the solution percolates through the slag pile. The fluoride reacts with the slag to precipitate calcium fluoride, which collects in the pile. The clear effluent from the pile, containing about 25-30 mg/l fluoride, discharges to the receiving ground water.

Phossy water from elemental phosphorus production contains substantial amounts of fluoride and elemental phosphorus which must be removed before the water is discharged to receiving waters or recycled to the process. Several processes have been used for treating the phossy water. The TVA has developed a treatment process which allows complete recycle of the treated phossy water (Figure 30). The phossy water is collected in a large storage tank where it is continuously agitated. A stream of the phossy water is fed to a clarifier where a flocculating agent is added. The suspended solids in the phossy water (including most of the phosphorus) are coagulated and removed as underflow from the clarifier. The supernate is pumped to a clarified water storage tank for recycle to the process. The underflow of solids and elemental phosphorus is centrifuged and the filtrate is returned to the phossy water system. The solids are burned to produce impure phosphoric acid. The treatment as described is quite effective in removing suspended solids and elemental phosphorus as the following data indicate:

Stream	Concentration - mg/l	
	Elemental Phosphorus	Suspended Solids
Phossy water	1700	2200
Clarified water	120	170

Dissolved solids build up in the clarified water as it recycles, and a bleed stream must be removed continuously to control the impurity levels. Typically the composition of the clarified recycle water will be:

Contaminant	mg/l
Phosphate	17,000
Sulfate	2,000
Fluoride	1,000
Ammonia	900
Phosphorus	120

The bleed stream amounts to about 6% of the clarified water flow. Most of the bleed stream is used to slurry the solids collected in the dust precipitators located in front of the phosphorus condenser (the slurried solids are recycled back to furnace feed preparation system). The remainder of the bleed stream is treated for dissolved solids removal by passing it over a bed of granulated furnace slag. The fluoride and phosphate react with the slag and precipitate. The solution percolates through the bed, solids are removed, and a clear effluent discharges from the slag pile. The effluent containing 10-30 mg/l fluoride, and <0.5 mg/l phosphorus is discharged to the receiving waters.

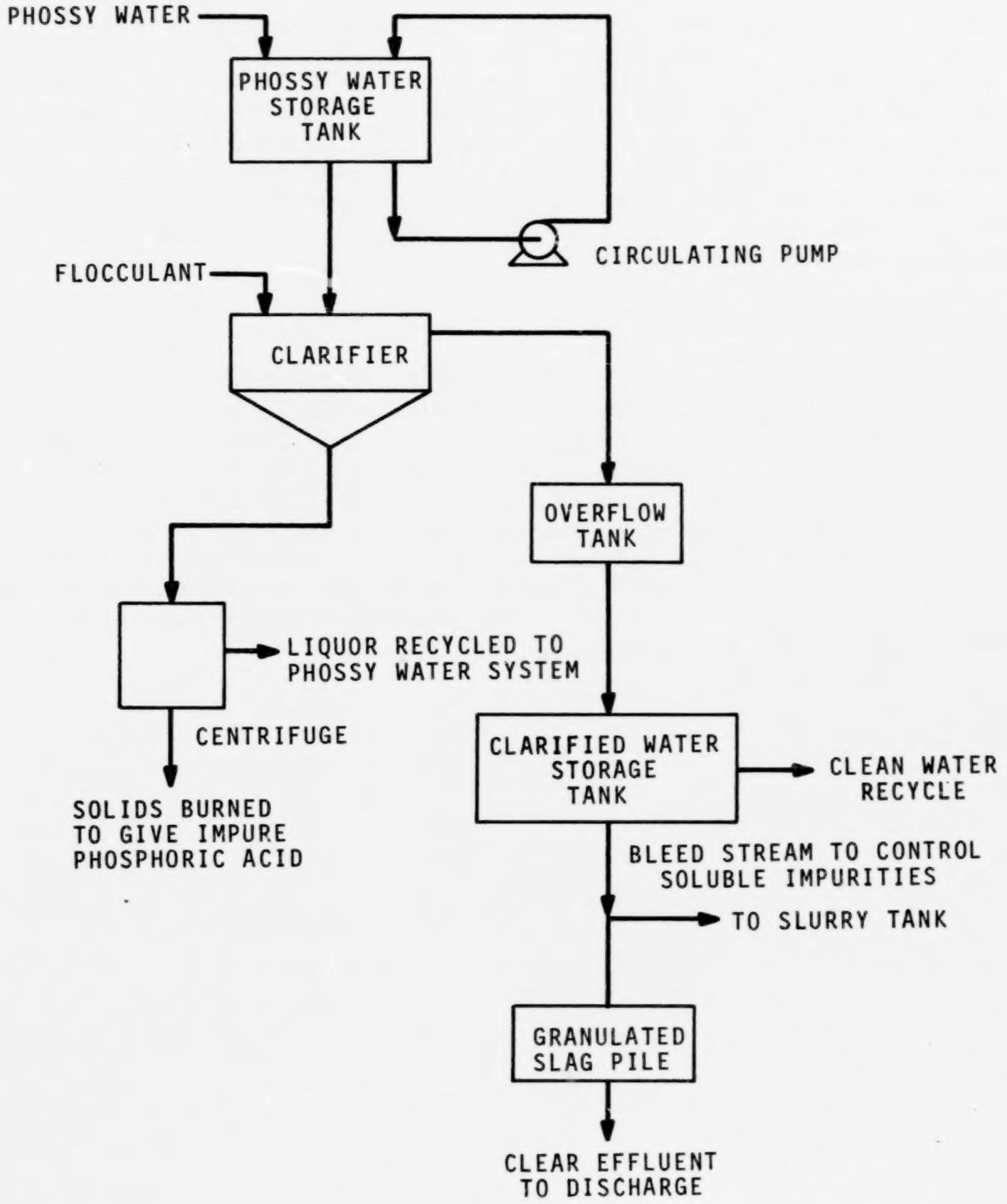
PHOSSY WATER
PHOSSY WATER STORAGE TANK
CIRCULATING PUMP
FLOCCULANT
CLARIFIER
OVERFLOW TANK
LIQUOR RECYCLED TO PHOSSY WATER SYSTEM
CENTRIFUGE
SOLIDS BURNED TO GIVE IMPURE PHOSPHORIC ACID
CLARIFIED WATER STORAGE TANK
CLEAN WATER RECYCLE
BLEED STREAM TO CONTROL SOLUBLE IMPURITIES
TO SLURRY TANK
GRANULATED SLAG PILE
CLEAR EFFLUENT TO DISCHARGE

FIGURE 30 TVA FLOWSHEET FOR TREATING PHOSSY WATER (50)

Other processes used for treating phossy water usually involve settling to allow the elemental phosphorus to separate out, followed by lime neutralization to precipitate the fluoride and phosphate. The solids are collected in a thickener and the clear supernate is discharged or recycled to the process. With good settling, the phosphorus content of the treated effluent is usually low enough to allow direct discharge to the ground waters. Sometimes, however, additional treatment is required to reduce the phosphorus to an acceptable level. This can be accomplished by oxidizing the elemental phosphorus with chlorine. Dissolved chlorine is quite toxic to aquatic life, however, so care must be used to control the chlorine addition. Oxidation with chlorine reduces the elemental phosphorus concentration below 0.5 mg/l.

POTASH INDUSTRY EFFLUENTS

Disposal of waste streams from potassium chloride production is not a problem. When the KCl is produced from brines, as happens at Bonneville and Searles Lake, any waste water streams produced are simply recycled back to a discharge area at the brine source. No treatment prior to discharge is required. Waste streams generated in the production of KCl from sylvinite are discharged to dumps where solar evaporation is used to remove the water. The solid waste remaining after evaporation accumulates at the dump. Normally, the waste streams are discharged to the dumps without treatment.

ECONOMICS OF EFFLUENT CONTROL

The economics of providing adequate treatment of fertilizer plant waste waters can have an important effect on fertilizer production. The cost required to meet water quality standards can ultimately affect the production processes used and the market value of the fertilizer products.

In evaluating the economic effects of effluent control on the fertilizer industry there are two factors which must be considered:

1. The capital and operating costs of treatment facilities required to meet water quality standards.
2. The cost of in-plant modifications designed to improve effluent control through reductions in waste loads and waste water volumes and increased waste water recycle.

Unfortunately, only a limited amount of information is available in the literature on the cost of treating fertilizer plant waste waters. Even less information is available on in-plant modifications. Overall, the fertilizer industry has done a good job of meeting current water quality standards. In most cases, however, they have failed to publicize their efforts to the extent that other industries have.

The cost data available on treatment of fertilizer plant waste waters are generally reported as total costs for the complete waste treatment system. These costs can vary over wide ranges depending on the type and degree of treatment used. Plant data obtained in the current study show the following typical cost ranges for treatment of ammonia and nitrogen fertilizer plant waste waters.

Product	Capital Cost ($/ton daily capacity)	Operating Cost ($/ton product)
Ammonia	200-1000	0.08-0.78
Ammonium Nitrate	150-600	0.06-0.50
Ammonium Sulfate	0-250	0-0.14
Urea	200-1000	0.08-0.68

The costs are due principally to oil separation and settling pond treatment. The low operating costs reflect the minimum treatment provided these waste streams.

In the production of wet process phosphoric acid the cost of treating gypsum pond water discharge by lime neutralization is reported to be \$0.80-\$1.80 per thousand gallons.(20) The cost per ton of P_2O_5 product is reported to be about \$1.50 for a 600 ton P_2O_5-per-day plant.(20) Data obtained in the current study show the operating costs varying from \$0.90-\$3.00 per ton of P_2O_5 product and average about \$1.90 per ton of P_2O_5 product. When no discharge from the gypsum pond is required the only operating costs involved are for pond maintenance and pumping.

Capital costs for gypsum ponds can vary over wide ranges because of the many variables involved in construction. A typical range of construction costs for ponds and related equipment as a function of plant size is shown in Figure 31.

Costs for treating phosphate fertilizer plant waste waters are largely dependent on how the scrubber solutions are handled. When the fluoride is recovered for sale, the value of the product approximates the cost of recovery. When the waste waters discharge to a gypsum pond the fertilizer plant product bears a proportionate share of the cost of treating the pond water dishcarge.

In phosphate fertilizer complexes approximately 11-15% of capital expenditure is for pollution control equipment and facilities. Of this amount 35-40% is for water pollution control.

A certain amount of data is available in the literature on unit costs for specific processes and operations within a waste treatment system. Those process data available which are relavent to fertilizer plant waste water treatment include data on oil separation, ammonia stripping, holding and settling ponds, and treatment of cooling water blowdown. Each of these operations is discussed in the following sections.

Oil removal from waste water is a significant problem in the fertilizer industry. Industry data on the cost of oil separation are lacking. However, there are considerable data in the literature on the cost of oil removal from petroleum refinery and other industrial waste waters. These data should apply to the treatment of fertilizer plant waste waters as well. Figure 32 shows typical capital costs and annual operating plus maintenance costs for API separators as a function of daily waste water flow. The data presented are for petroleum refinery waste water treatment.(10,70) The costs should not be significantly different for fertilizer plant waste water treatment.

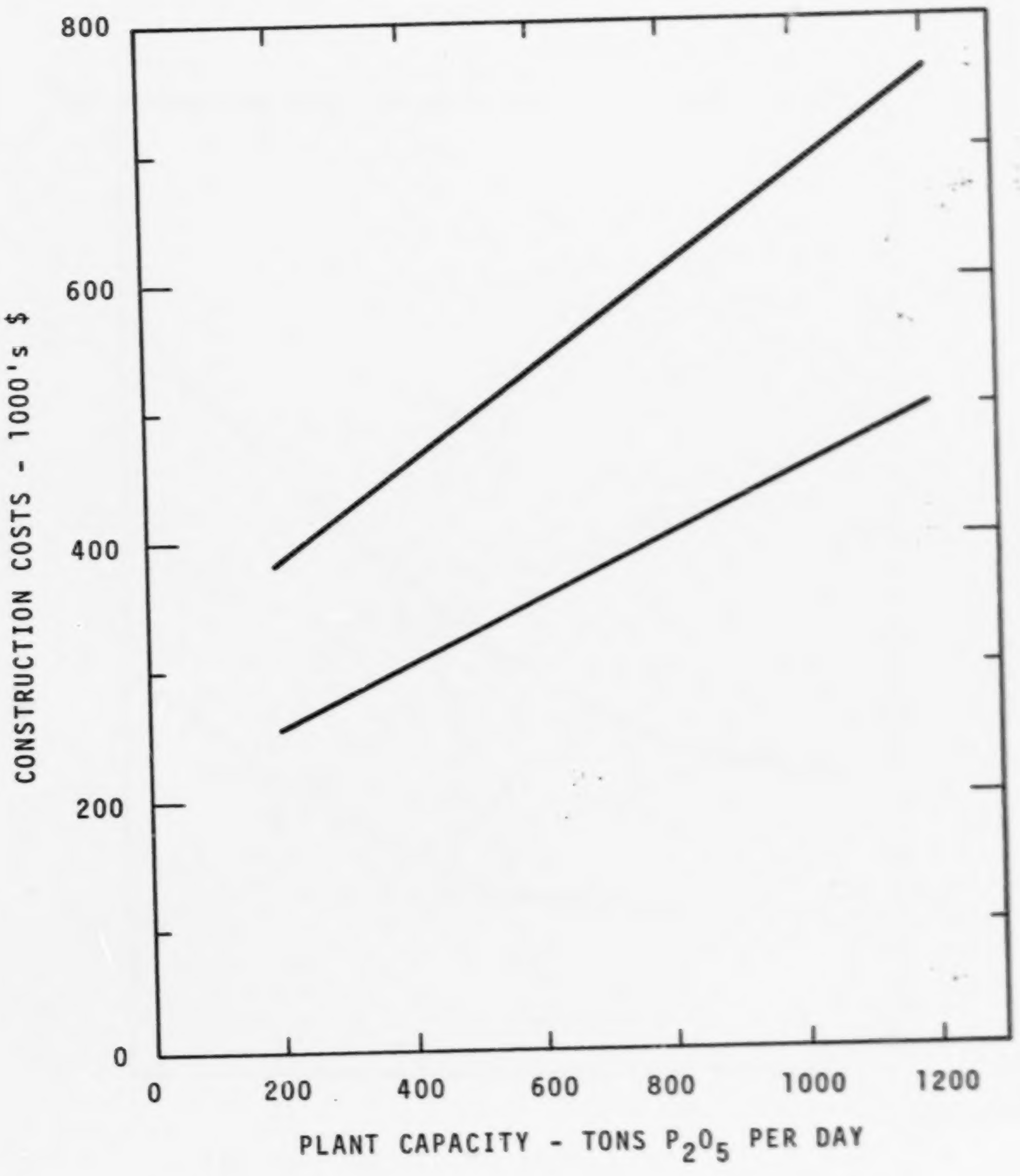

FIGURE 31 TYPICAL GYPSUM POND CONSTRUCTION COSTS

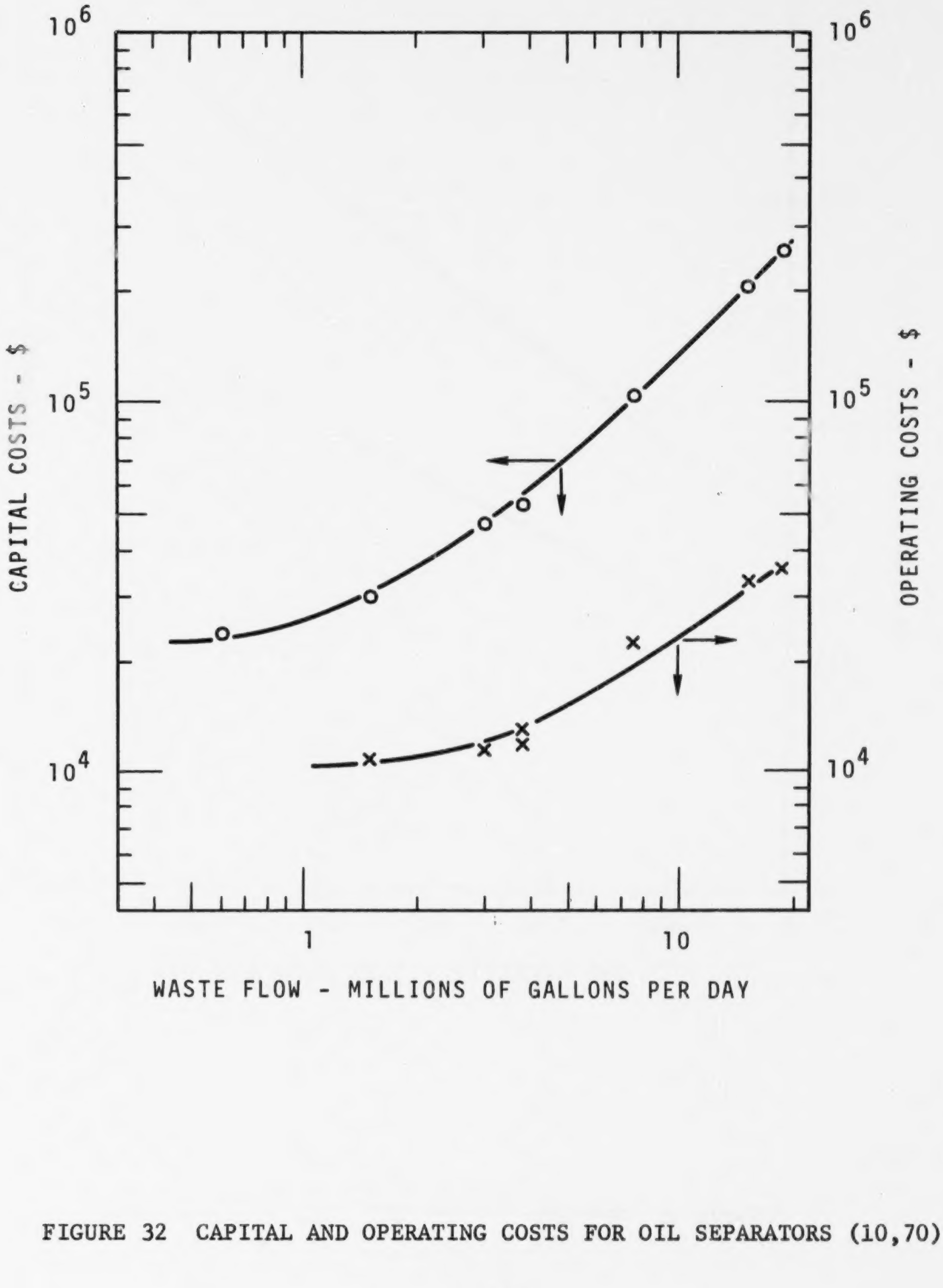

FIGURE 32 CAPITAL AND OPERATING COSTS FOR OIL SEPARATORS (10,70)

Air flotation removal of oil is somewhat more expensive. Capital costs are approximately twice those of API separators and operating and maintenance costs are about 1.5 times as high.(70)

Many fertilizer plants make use of holding or settling ponds for storing waste waters prior to discharge. The capital cost of settling or holding ponds is dependent on a number of factors such as plant location, land availability, etc. Figure 33 shows a typical range of construction costs for ponds as a function of pond area. Pond maintenance and operating costs are normally very low.

Very little cost data are available on the stripping of ammonia from fertilizer plant waste waters. The capital cost of an ammonia stripper and condenser for a 1200 ton per day ammonia plant is reported to be \$60,000.(66) Ammonia strippers used in the petroleum industry and capable of handling approximately the same waste flows cost in the range of \$40,000-\$60,000. Operating costs for ammonia strippers are difficult to predict since costs depend primarily on the degree of ammonia removal required. Data on ammonia removal from secondary sewage effluent by stripping show the operating costs to be about \$0.05/1000 gallons treated to achieve about 80% ammonia removal.(71)

Treatment of cooling tower blowdown is normally required to remove chromate corrosion inhibitor. Chromate destruction is usually achieved by treating the blowdown waste with SO_2 and lime. Table 16 summarizes typical cost data for removing chromate from blowdown waste water using SO_2 and lime.(72)

TABLE 16

TYPICAL COST DATA FOR CHROMATE REMOVAL FROM COOLING WATER BLOWDOWN(72)

Inhibitor System	Initial Concentration (mg/l)	Concentration In Treated Waste (mg/l)	Disposal Cost (\$/1000 gallons)
Chromate only	200-500	CrO_4-0.05 Cr -3.0	0.70
Zinc Chromate	8-35 17-65	CrO_4-0.05 Cr -3.0 Zn -5	0.16
Zinc Chromate Phosphate	8-35 10-15 30-45	CrO_4-0.05 Cr -3.0 Zn -5	0.13

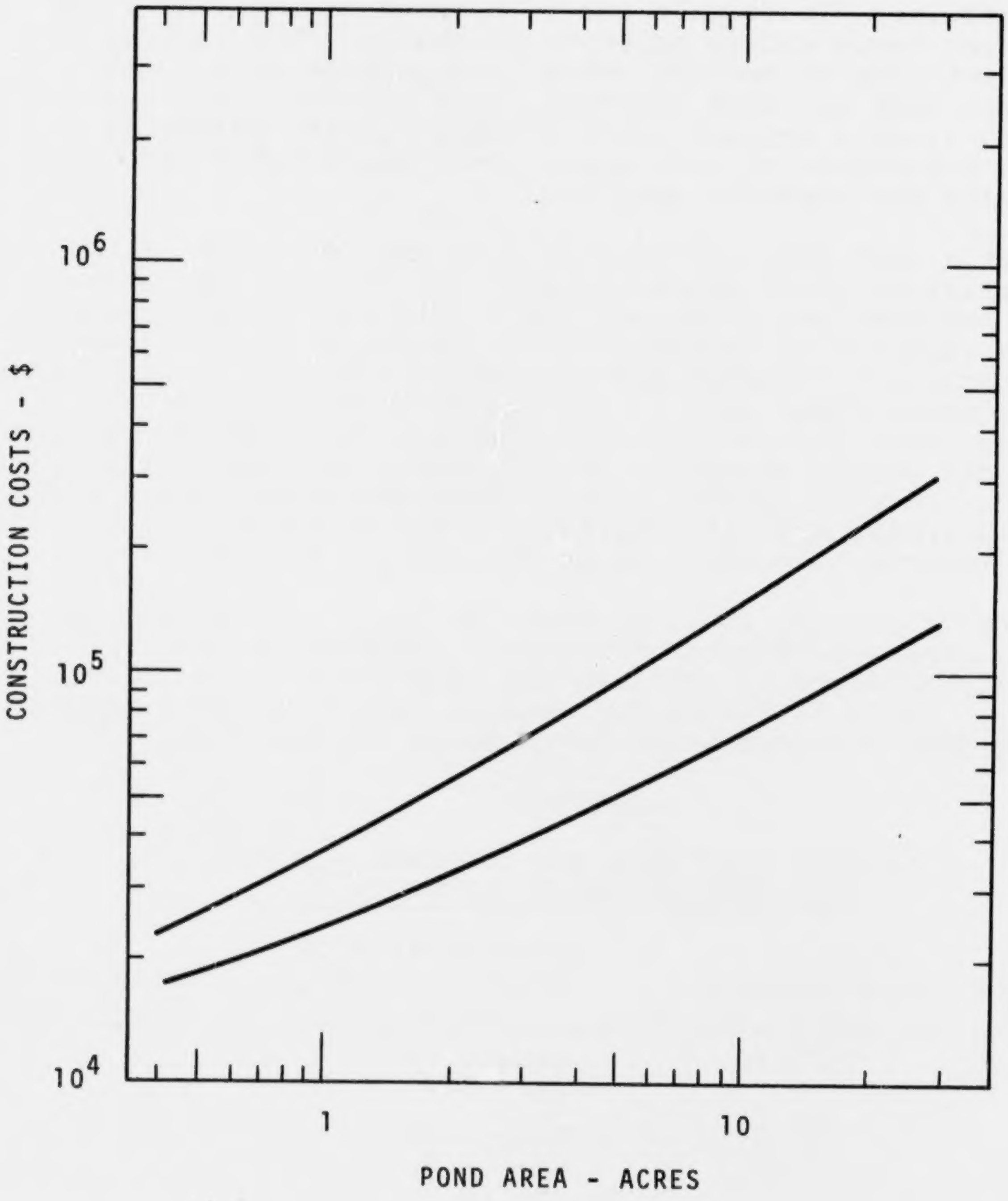

FIGURE 33 TYPICAL CONSTRUCTION COSTS FOR HOLDING AND SETTLING PONDS

The estimated capital equipment costs for a plant to treat 100 gpm of blowdown waste are presented in the following table.(72)

Inhibitor System	Capital Cost
Chromate	$25,000
Zinc-chromate	30,000
Zinc-chromate-phosphate	31,000

When organics are present in the blowdown streams (i.e., organic phosphate corrosion inhibitors and biocides) other treatment methods are required and treatment costs may be substantially higher.

RESEARCH AND DEVELOPMENT REQUIREMENTS FOR REQUIRED CONTROL OF AQUEOUS EFFLUENTS

The technology is currently available for controlling many of the pollutants found in fertilizer plant waste streams. There are, however, certain problem areas where additional development effort is needed to provide feasible waste treatment methods. In addition, it is almost a certainty that water quality standards will become more restrictive in the future. Waste treatment methods which are sufficient for current water quality standards may not be satisfactory for meeting future standards. This means new waste treatment technology will have to be developed for those situations where current technology may prove inadequate.

Following is a list of current and potential problem areas which need investigation to assist the fertilizer industry in maintaining adequate control over aqueous effluents. (No significance should be placed on the order in which the problem areas are discussed.)

1. Realistic Water Quality Standards - The basic problem facing the fertilizer industry in regard to waste water pollution control is the assurance that future water quality standards will be both realistic and reasonable, particularly with regard to the nutrient content of waste waters. Unrealistic standards for nitrogen, phosphate and fluoride could have a disastrous effect on future fertilizer production. A program is needed which will permit definition of realistic standards for those pollutants of primary interest to the fertilizer industry.

2. Ammonia Removal - The use of dilution as a means of controlling ammonia bearing waste waters is unacceptable in some areas today, and will be less acceptable in the future. Economic treatment methods for ammonia removal from fertilizer plant waste waters are needed. A number of processes have been studied for ammonia removal from waste water. In most cases, however, the processes have been applied to the removal of ammonia from sewage. With the exception of stripping, none are currently being applied to fertilizer plant waste waters. Selective ion exchange for ammonia removal appears to be the most attractive method currently available for treating fertilizer plant waste waters.(41) A much needed program (supported by the EPA under Grant No. 12020 EGM) is currently underway at the Farmers Chemical Association, Inc. plant at Tyner, Tennessee to evaluate the use of ion exchange

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for removing ammonia and nitrate from fertilizer plant waste waters. However, the magnitude of the ammonia problem justifies additional ion exchange studies. Application of other ammonia removal methods to fertilizer plant waste waters should also be evaluated.

3. Nitrogen Removal - Methods are also needed for the removal of other forms of nitrogen from fertilizer plant waste waters, particularly nitrate and urea. As is the case with ammonia, dilution is still the basic means of control for nitrate and urea. If dilution becomes unacceptable, as appears likely, there are no demonstrated treatment methods available for removing nitrate and urea from fertilizer plant waste waters. The Farmers Chemical Association study on ammonia and nitrate removal by ion exchange may prove satisfactory for nitrate removal. However, studies should be undertaken to develop a suitable method for urea removal.

4. Gypsum Utilization - Gypsum produced in phosphoric acid manufacture is not usually considered a major disposal problem. It is simply allowed to accumulate in the gypsum pond. However, considerable land area is required to accommodate the large tonnages of by-product gypsum turned out by the phosphate industry each year. In areas where phosphoric acid manufacture is heavily concentrated, such as central Florida, the land required for gypsum disposal can become very large. Various methods for utilizing the by-product gypsum have been studied in the past and in most cases have been found to be uneconomical. It would appear, however, that additional efforts to develop ways of utilizing the gypsum are needed and are economically justified.

5. Fluoride Removal - Fluoride is a principal contaminant in all waste waters discharge from phosphoric acid and phosphate fertilizer plants. Lime neutralization, when combined with dilution, provides sufficient fluoride removal to meet current fluoride water quality standards. It appears quite likely, however, that fluoride standards will become more restrictive. It is very doubtful that lime neutralization would provide the fluoride removal needed if the fluoride standards are reduced much below their current levels. Therefore, a program should be undertaken to develop alternate methods of fluoride removal and possible recovery.

6. Phosphate Removal - Lime neutralization is also used for phosphate removal from fertilizer plant waste waters. The treatment, combined with dilution, is sufficient to meet current phosphate standards, but will not be satisfactory if phosphate standards are reduced significantly. A suitable alternative to lime neutralization should be developed.

   A variety of processes has been developed for phosphate removal from sewage.(73,74,75,76) Most of these processes will reduce the phosphate to quite low levels. Application of these processes to the treatment of fertilizer plant waste waters should be investigated for both technical and economic feasibility.

7. Lime Neutralization Mechanism - When phosphate is precipitated by lime neutralization the precipitated species at pH 6 and above is reported to be hydroxyapatite [$Ca_5OH(PO_4)_3$]. The reported solubility of the hydroxyapatite is extremely low. However, the concentration of phosphate in neutralized gypsum pond water is relatively high ($\geq$10 mg/l). An investigation of the precipitation mechanism and phosphate species present could lead to improvement in the lime neutralization process and extend its usefulness.

8. Continuous Monitoring Procedures - With the exception of pH measurement, reliable continuous analytical methods for monitoring the principal contaminants found in fertilizer plant waste waters are not available. Development of continuous methods for fluoride, phosphate, ammonia and nitrate analysis would greatly assist the fertilizer industry in controlling waste water discharge. Process leaks and malfunctions could be more easily detected, and process losses could be reduced.

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PART II PHOSPHATE ROCK MINING AND BENEFICIATION

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PHOSPHATE ROCK MINING AND BENEFICIATION

INTRODUCTION

Phosphorus, one of the major plant food elements, is obtained in the United States from sedimentary deposits of phosphate rock. Current production capacity of phosphate rock is approximately 50 million short tons of material mined. In 1970, the actual production of phosphate rock was about 39 million short tons. Total world production of phosphate rock in 1970 was about 89 million short tons.(1) The United States is by far the major current world producer of phosphate rock. The United States exported about 11.3 million short tons of phosphate rock; thus, the major amount of that mined in the United States is used domestically for production of phosphoric acid, either by wet acid processing or by production of elemental phosphorus in an electric furnace.

Phosphate mining operations are conducted in but eight of the states. In order of production capacity, these are Florida, Tennessee, North Carolina, Idaho, Montana, Utah, Wyoming, and California. Almost 80 percent of the production capacity is in the state of Florida. For that reason, more emphasis has been given in this study to the operating practices in the southeast and particularly in Florida.

Production of phosphate rock for acid manufacture involves mining and physical beneficiation of the mined rock to concentrate the phosphate values. These operations are generally done by hydraulic mining and washing methods involving usage of tremendous amounts of circulating water. For the most part, the water used in the mining and beneficiation of phosphate rock is recirculated with evaporation losses made up with fresh water. However, because vast amounts of water are retained with the solids rejected from the washing and beneficiation operations, there are inherent problems in the handling of these rejects that relate to the water ecology of the region and to potential sources of water pollution.

The purpose of this phase of the study was to review current practices involved in the mining and beneficiation of phosphate rock in relation to possible water pollution aspects and to report on progress and plans for alleviating problems being faced by this industry.

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SUMMARY

A review was made of the phosphate mining and beneficiation practice in the United States in relation to the effluents generated by these operations and the potential water pollution problems involved.

The major effluent from phosphate mining and beneficiation is the discharge of water suspensions of sand tailings and phosphate containing slime solids. These discharges are wholly contained within the mined out areas and in carefully constructed slime ponds; therefore, these wastes from the mining and beneficiation operations are not discharged to the environment. However, clarified water from the ponds is discharged periodically during periods of heavy rainfall to maintain a safe level of water in the slime ponds. There is no reported evidence that any components in this discharge, either dissolved or suspended, have an adverse effect on the ecology of the surrounding water shed, with the possible exception of trace nutrients which promote growth of algae.

Although the effluents from the mining and beneficiation operations were not found harmful in the concentrations characteristic of these operations, the problem of disposal, particularly of slimes disposal, is a severe problem to the industry. The potential hazard of dam breakage is always present and damages through sudden spillage of slimes into surrounding waterways are documented by a history of such occurrences. Moreover, slimes disposal by present methods means a constant demand for large amounts of fresh water. This is a drain on the aquifer or water resource of the area.

Although the phosphate slimes disposal problem is one that is well known by the industry and has received attention by the operators and by various government research and development agencies, the problem is largely a regional problem. For that reason the magnitude of this disposal problem, particularly from the standpoint of water and land usage, has not generally been recognized by the public. Despite extensive research through the years by both industry and government, the problem of improving the means to dewater or otherwise dispose of these effluents remains, which attests to the limitations of present technology and the economic factors invovled. For these reasons, it is recommended that a coordinated research activity be established to continue to investigate various possible methods that prior work has indicated can provide potential solutions to the slimes problem. The specific areas for this research are recommended in this report.

THE PHOSPHATE ROCK INDUSTRY

Phosphorus, one of the major plant food elements, is mined in the United States almost entirely in the form of phosphate rock from sedimentary deposits. Three-fourths of the phosphate rock mined in the United States is used in agriculture in fertilizer form. The remainder is used to make phosphoric acid-based chemicals. Phosphate chemicals are used in bone meal for animal feed, detergents, water softeners, rust proofing, flame-resisting compounds, and for several other minor uses.

Phosphate rock production decreased by 3.2 percent in 1969(2) and remained at the 1969 level during 1970.(1) The decrease in the production of phosphate in the United States was the first decline since 1957.(2) However, expansion is expected to resume in the next few years. TVA anticipates a rise of some 18 percent in capacity between 1970 and 1975.(2) A balance between supply and demand in the United States is expected by 1972 and an annual growth rate of some 4 to 5 percent is anticipated thereafter.(2) Table 17 presents the estimated production of phosphate rock in the United States.(3) Based on these estimates, the resources of phosphate rock in the United States would last some 45 to 64 years.(3) If the low-grade rock could be used, the duration of availability of phosphate rock would be about 7 times greater.(3)

TABLE 17

ESTIMATED PRODUCTION OF MARKETABLE PHOSPHATE ROCK IN THE UNITED STATES(3)

(Thousands of Short Tons)

Year	Projection Range	Phosphate Rock	P_2O_5 Content
1965	---	39,436 (a)	9,132 (a)
1966	---	39,044 (a)	12,112 (a)
1967	---	39,770 (a)	12,464 (a)
1985	Low	68,000	21,000
	Medium	87,000	27,000
	High	102,000	32,000
2000	Low	96,000	30,000
	Medium	160,000	50,000
	High	208,000	65,000

(a) Actual

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THE NATURE OF PHOSPHATE MINERALS AND DEPOSITS

Phosphate rock does not have a definite chemical composition and phosphate deposits may contain one or more phosphate minerals. The principal minerals have the apatite structure and have a generalized formula of $3Ca_3P_2O_8 \cdot CaF_2$. This formula shows a theoretical content of 92.25 percent tricalcium phosphate, $Ca_3P_2O_8$, or bone phosphate of lime (BPL) as it is commonly called. The beneficiated rock in marketable form usually contains 68 to 77 percent BPL. Table 18 illustrates the extremes in composition of the phosphate rock$^{(4)}$ showing substitutions of such elements as Mg and Na.

TABLE 18

VARIATIONS IN PHOSPHATE ROCK COMPOSITIONS

Component	Composition Range, percent by weight	
CaO	55.6	55.1
MgO	0.0	0.7
Na_2O	0.0	1.4
P_2O_5	42.2	33.95
CO_2	0.0	6.3
F	3.77	5.04

The apparent hardness of phosphate rock varies from 2 to 5 (Mohs scale). Structures include hard rock, granular, and a loosely consolidated earthy mass.

In Florida the phosphate deposit occurs principally as a loose consolidated conglomerate mixed with sand and clay, within a region about 30 miles in diameter in Polk and Hillsborough Counties. The North Carolina deposit occurs as interbedded phosphatic clays, limestones, and sands covering approximately a 700 square mile area in eastern Beaufort County. The Tennessee brown rock deposits are a weathered phosphatic limestone, that occurs in a north-south trending belt across the state passing through Nashville and Columbia. The western phosphates occur as a folded and faulted shale member of the Permian Phosphoria formation covering an area 350 miles north and south by about 100 miles wide in portions of Montana, Idaho, Wyoming, and Utah.

MINING PHOSPHATE ROCK

Florida, Tennessee, and North Carolina account for 86 percent of the United States phosphate rock mine production.(3) Figure 34 shows the location of the commercial phosphate rock deposits. Table 19 gives the actual location and tonnage capacity of phosphate rock mining operations in the United States.(6)

Most phosphate rock is mined by open-pit methods. The general practice is to strip the overburden with electric-powered draglines and then remove the phosphate rock. The mined rock, referred to as matrix, is then placed into a previously prepared sluice pit. Hydraulic monitors developing 200 psi pressure and using as much as 10,000 to 12,000 gpm of water break up the matrix and slurry it at approximately 40 percent solids into the suction end of large centrifugal dredge pumps. The matrix is then pumped through movable steel pipelines for distances of up to 6 miles to the beneficiation plant.

Although phosphate rock is mined in some locations in the West by underground techniques rather than by open-pit methods, such operations account for only a minor part of the total production.

The common practice in Florida and North Carolina is to strip the overburden and place it in windrows along side the cut. The overburden is then bulldozed to build the dams for the slime ponds. The cuts are usually about 125 to 200 feet in width and several hundred feet long, depending upon the size of the dragline.

After the overburden is removed, the ore is placed into sluice pits where hydraulic monitors break up the ore and slurry it into the suction of large dredge pumps. The matrix is pumped through large steel lines to the beneficiation plant. The beneficiation plant is usually located within 6 miles of the mining area.

The open-pit mining in Tennessee and the Western States is somewhat different in that it is common practice to remove the overburden well in advance of the actual mining operations. Also, the matrix, when mined, is loaded into trucks or railroad cars and hauled to washer plants instead of being pumped.

The underground deposits of the Western phosphates generally are mined by the room-and-pillar method. Figure 35 illustrates a typical room-and-pillar mining method. Other underground mining methods that have been utilized to a limited extent include shrinkage stopping, top slice, cut-and-fill, and long-wall stopping.

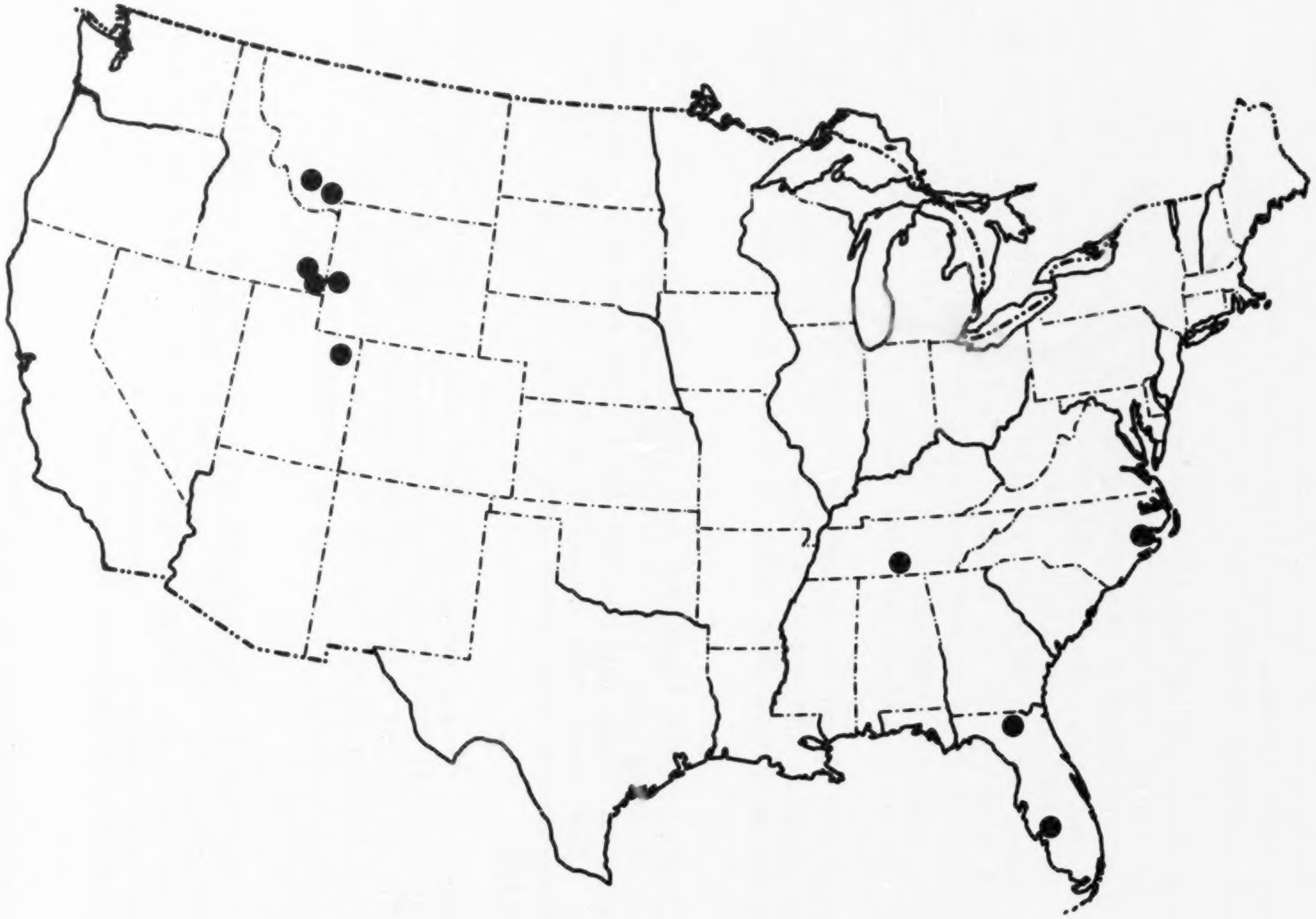


FIGURE 34 GEOGRAPHICAL LOCATION OF PHOSPHATE ROCK OPERATIONS

TABLE 3

PHOSPHATE ROCK MINES IN THE UNITED STATES(6)

Company	Location	Capacity, 1000 Short Tons Year Ending		
		1968	1969	1970
American Cyanamid Company	Brewster, Florida	3,650	3,650	3,650
Borden Chemical Company	Teneroc, Florida	1,500	1,500	1,500
Cominco-American, Inc.	Douglas, Montana	750	750	750
	Garrison, Montana			
Continental Oil Company	Pierce, Florida	6,500	6,500	6,500
Cuyama Phosphate Corporation	Cuyama, California	300	300	300
El Paso Natural Gas Co.	Soda Springs, Idaho	400	400	400
W.R. Grace & Company	Bonny Lake, Florida	1,550	1,550	1,550
International Minerals & Chem. Corp.	Bonnie, Florida	6,000	6,000	6,000
	Kingsford, Florida	2,000	2,000	2,000
Mobil Chemical Company	Fort Meade, Florida	5,700	5,700	5,700
	Mt. Pleasant, Tenn.	200	200	200
Monsanto Company	Ballard, Idaho	1,000	1,000	1,000
	Columbia, Tenn.	1,000	1,000	1,000
Mountain Fuel Supply Co.	Conda, Idaho	250	250	250
Occidental Chemical Co.	White Springs, FL	3,000	3,000	3,000
Occidental Chemical Co. - Hooker	Columbia, Tennessee	750	750	750
Presnell Phosphate Co.	Columbia, Tennessee	700	700	700
George Relyea	Garrison, Montana	100	100	100
J.R. Simplot Company	Fort Hall, Idaho	1,000	1,000	1,000
	Soda Springs, Idaho			
Stauffer Chemical Company	Melrose, Montana	600	600	600
	Hot Springs, Idaho	200	200	200
	Montpelier, Idaho			
	Vernal, Utah	200	200	200
	Cherokee, Utah	400	400	400
	Leefe, Wyoming	500	500	500
	Mt. Pleasant, Tenn.	600	600	600
Swift & Company	Watson, Florida	3,000	3,000	3,000
	Silver City, FL			
Tennessee Corporation-USPP	Fort Meade, FL	2,000	2,000	2,000
Tennessee Valley Authority	Knob Creek, Tenn.	200	200	200
	Franklin, Tenn.			
Texas Gulf Sulphur Corp.	Lee Creek, NC	3,000	3,000	3,000
U.S.S. Agri. Chemicals-Armour	Armour, Florida	1,500	1,500	1,500
	Lake Hancock, FL			
	Fort Meade, Florida	---	2,000	2,000
	Columbia, Tenn.	90	90	90
TOTAL UNITED STATES		48,640	50,640	50,640

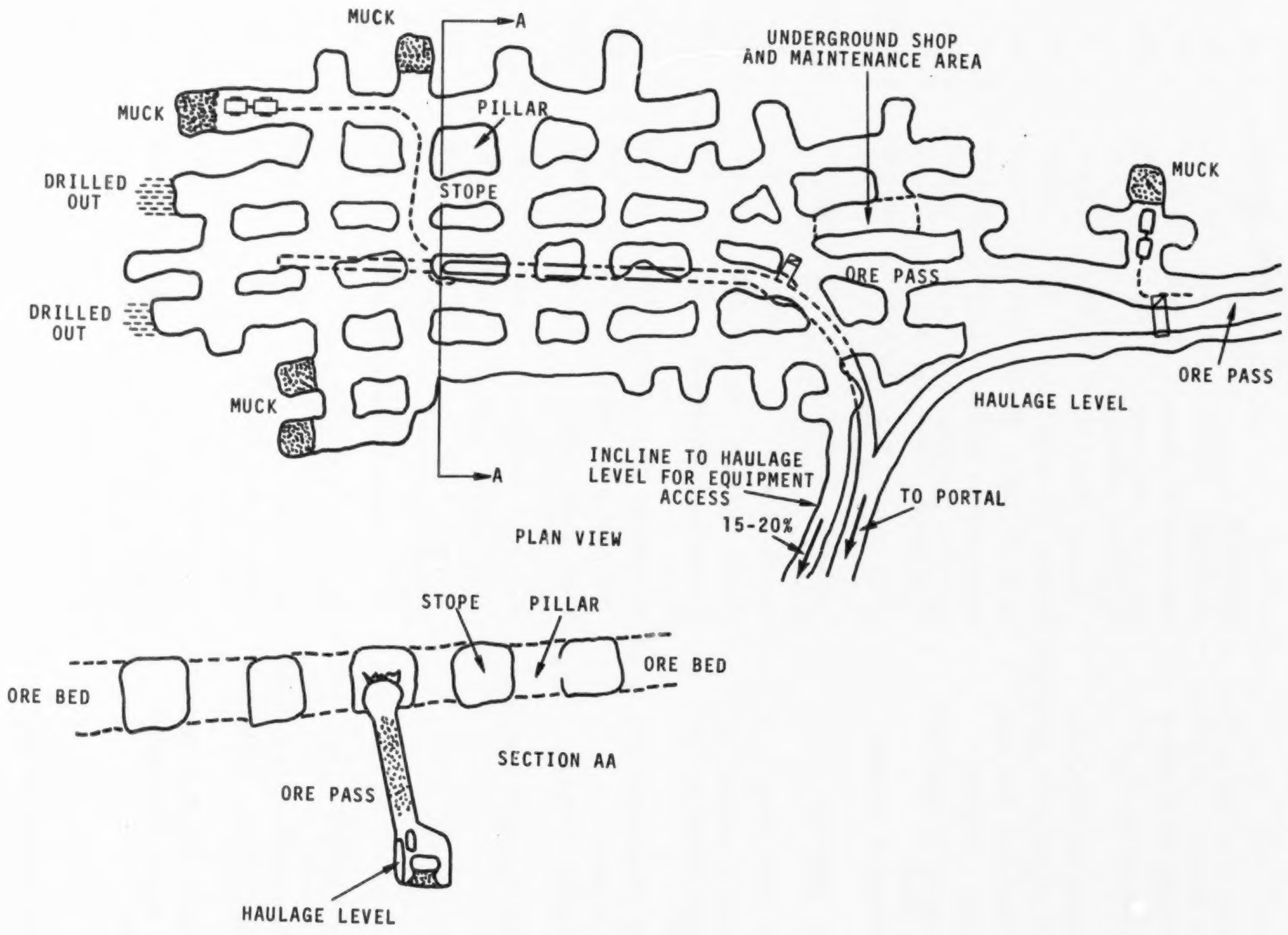

MUCK
A
UNDERGROUND SHOP AND MAINTENANCE AREA
MUCK
PILLAR
MUCK
DRILLED OUT
STOPE
ORE PASS
DRILLED OUT
ORE PASS
HAULAGE LEVEL
MUCK
INCLINE TO HAULAGE LEVEL FOR EQUIPMENT ACCESS
A
TO PORTAL
15-20%
PLAN VIEW
STOPE
PILLAR
ORE BED
ORE BED
SECTION AA
ORE PASS
HAULAGE LEVEL

FIGURE 35 GENERAL PLAN FOR CONVENTIONAL ROOM-AND-PILLAR MINING

BENEFICIATING PHOSPHATE ROCK

The methods of beneficiation of phosphate rock differ to some extent with each operating company. Important factors related to the methods used include: the size and analysis of the matrix; the ratio of phosphate, clay, and sand in the matrix; and preference by the operator for certain equipment. In general, the first treatment step is the separation of coarse phosphate rock from the clay, sand, and fine phosphate; this is accomplished in a washer plant. The washer plant separates the matrix into three components: slimes, fine phosphate and sand, and coarse phosphate. A generalized flowsheet for the beneficiation operation is shown in Figure 36. A diagram showing the approximate distribution of products from the beneficiation operation is provided in Figure 37.

It can be noted from the general beneficiation plan shown in Figure 36 that the coarse phosphate removed at the washer is stockpiled as a marketable product. The fine material consisting of sands, clay, and fine phosphate is generally deslimed to remove clays then sent to the flotation plant where the fine phosphate is removed by flotation. The reminder of the material is then discarded and referred to as sand tails. The slimes, containing only 4 to 6 percent solids, are generally pumped to slime ponds that have been constructed in the mined out areas.

It is important to note that the slimes account for one-third of the total tonnage of matrix mined. Thus, about one-third of the phosphate values is currently lost as phosphate slimes. It is also important to note that the volume of these slimes is from 25 to 100 percent greater than the matrix that is mined. Therefore, the disposal of the slimes cannot be done within the mined out areas except by construction of dams to contain the increased volume. Dams are constructed to retain slimes to depths of up to 40 feet. The water leaving the plant with these slimes amounts to about one-half the water requirements of the mining and beneficiation operation.

As noted previously, the beneficiation operations vary with location and operator. Generalized flowsheets which illustrate the plans used in Florida, North Carolina, Tennessee, and the Western states are provided in Figures 38 through 43 (2)

It can be noted by review of these flowsheets that, in general, the 1-inch by 14 mesh is the washer rock product; the underflow from the washer is deslimed at 150 mesh with the minus 150 mesh material being pumped to waste. The deslimed product is then split into two sized fractions, one 14 by 35 mesh for gravity concentration and the other 35 by 150 mesh for

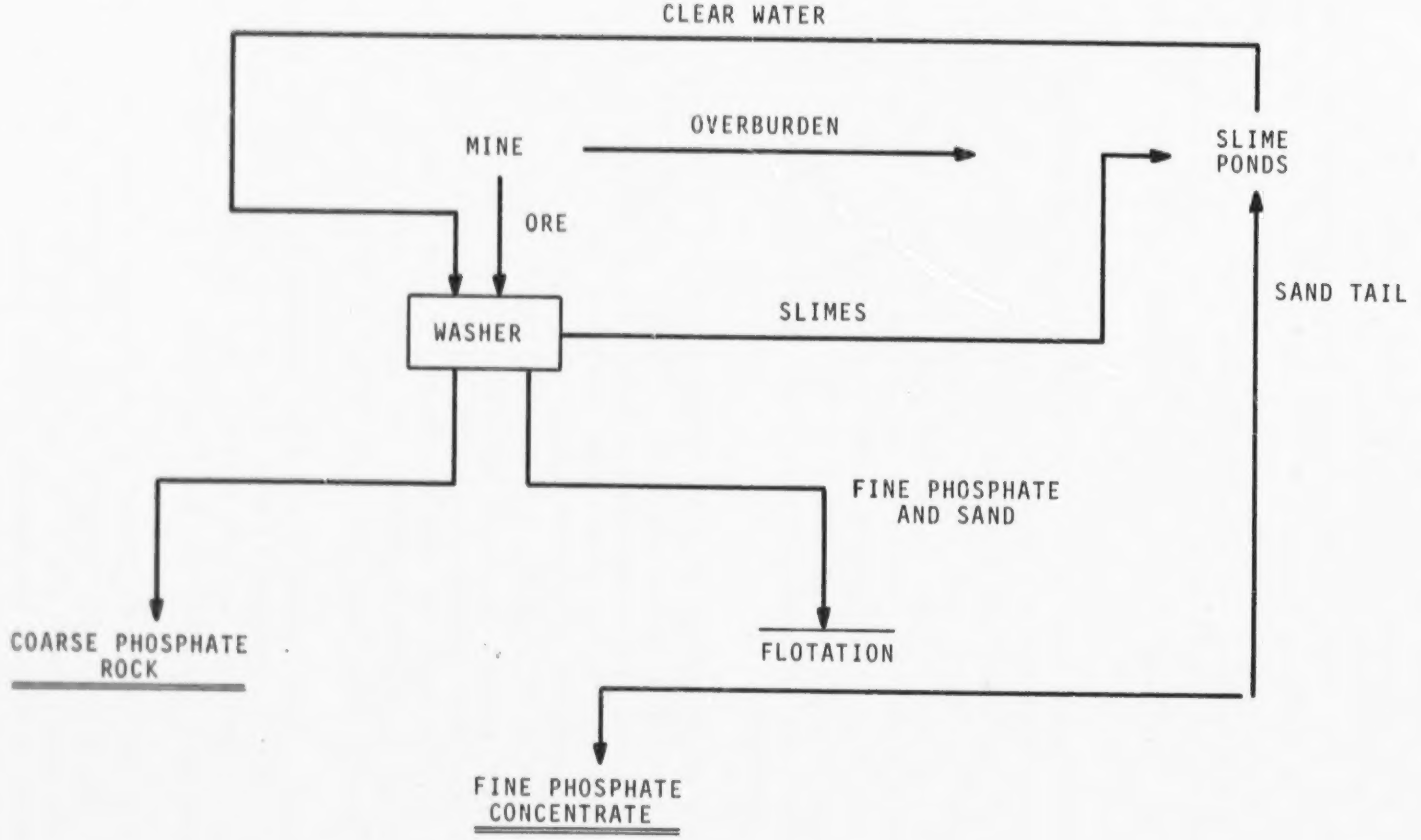
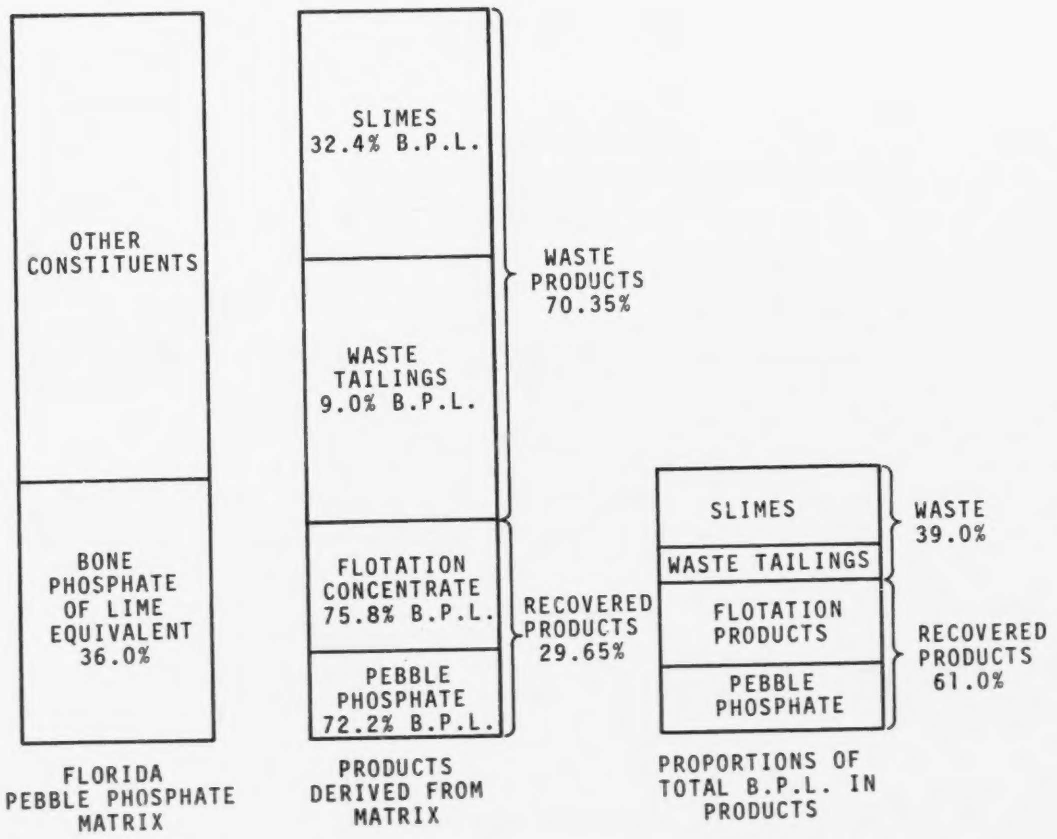

CLEAR WATER
MINE
OVERBURDEN
ORE
SLIME PONDS
WASHER
SLIMES
SAND TAIL
FINE PHOSPHATE AND SAND
COARSE PHOSPHATE ROCK
FLOTATION
FINE PHOSPHATE CONCENTRATE

FIGURE 36 GENERALIZED FLOWSHEET OF A PHOSPHATE ROCK MINING AND BENEFICIATION PLANT



OTHER CONSTITUENTS
BONE PHOSPHATE OF LIME EQUIVALENT 36.0%
FLORIDA PEBBLE PHOSPHATE MATRIX
SLIMES 32.4% B.P.L.
WASTE TAILINGS 9.0% B.P.L.
WASTE PRODUCTS 70.35%
FLOTATION CONCENTRATE 75.8% B.P.L.
PEBBLE PHOSPHATE 72.2% B.P.L.
RECOVERED PRODUCTS 29.65%
PRODUCTS DERIVED FROM MATRIX
SLIMES
WASTE TAILINGS
WASTE 39.0%
FLOTATION PRODUCTS
PEBBLE PHOSPHATE
RECOVERED PRODUCTS 61.0%
PROPORTIONS OF TOTAL B.P.L. IN PRODUCTS

FIGURE 37 DISTRIBUTION OF PRODUCTS DERIVED FROM LAND-PEBBLE PHOSPHATE ROCK, percent

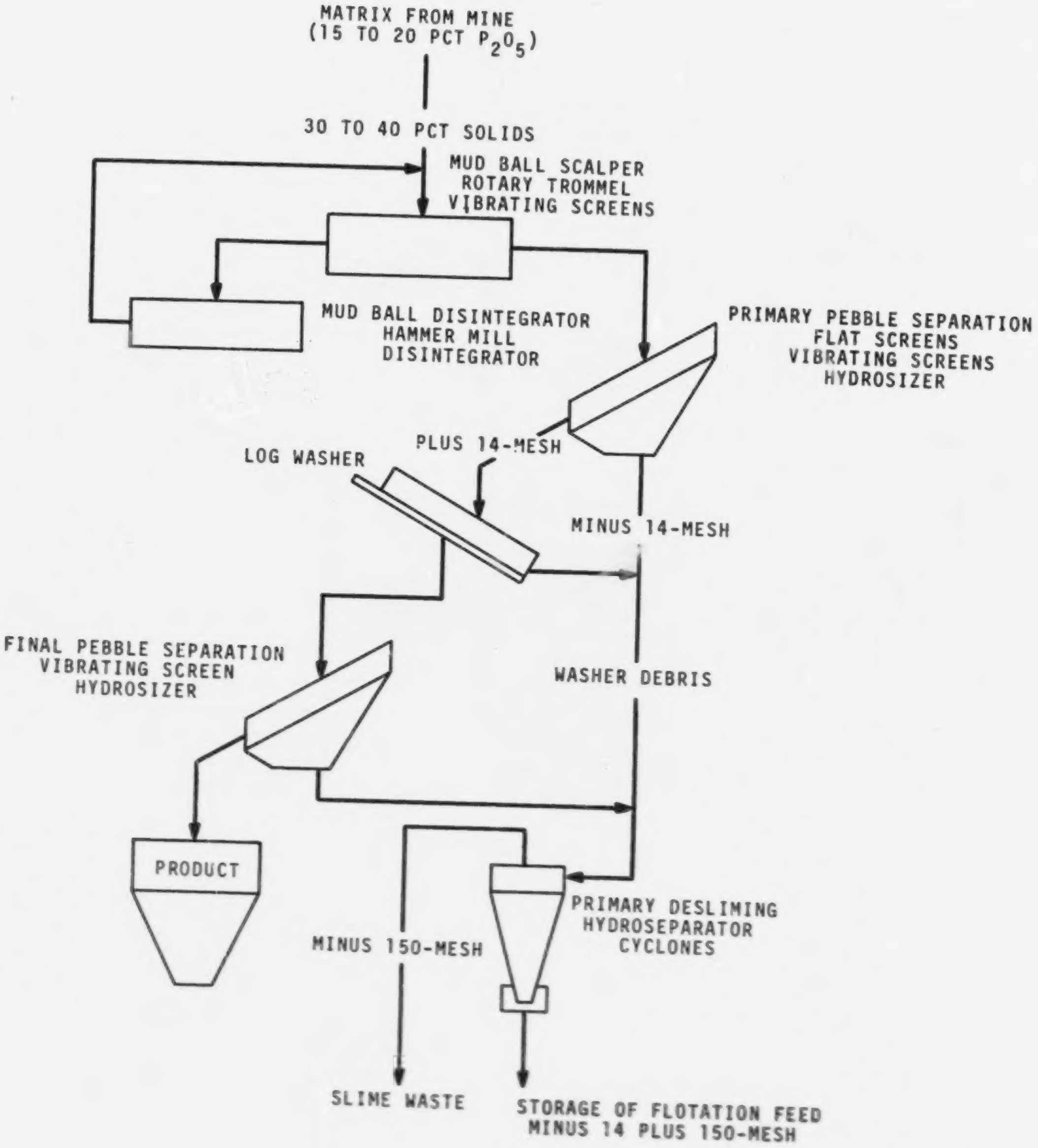

MATRIX FROM MINE
(15 TO 20 PCT P_2O_5)
30 TO 40 PCT SOLIDS
MUD BALL SCALPER
ROTARY TROMMEL
VIBRATING SCREENS
MUD BALL DISINTEGRATOR
HAMMER MILL
DISINTEGRATOR
PRIMARY PEBBLE SEPARATION
FLAT SCREENS
VIBRATING SCREENS
HYDROSIZER
PLUS 14-MESH
LOG WASHER
MINUS 14-MESH
FINAL PEBBLE SEPARATION
VIBRATING SCREEN
HYDROSIZER
WASHER DEBRIS
PRODUCT
PRIMARY DESLIMING
HYDROSEPARATOR
CYCLONES
MINUS 150-MESH
SLIME WASTE
STORAGE OF FLOTATION FEED
MINUS 14 PLUS 150-MESH

FIGURE 38 GENERALIZED FLOWSHEET OF A WASHER PLANT FOR RECOVERING FLORIDA PEBBLE PHOSPHATE

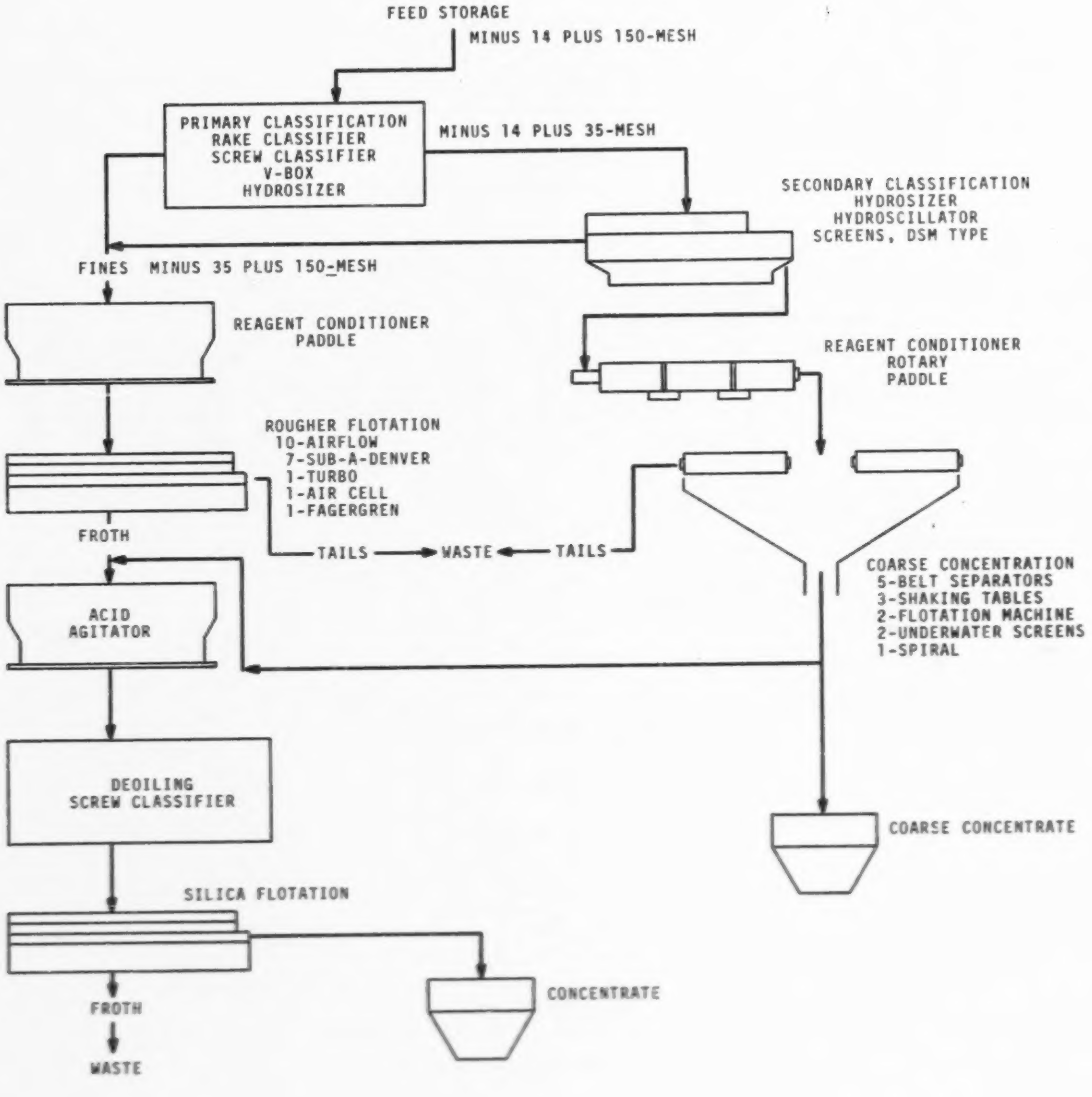

FEED STORAGE
MINUS 14 PLUS 150-MESH
PRIMARY CLASSIFICATION
RAKE CLASSIFIER
SCREW CLASSIFIER
V-BOX
HYDROSIZER
MINUS 14 PLUS 35-MESH
SECONDARY CLASSIFICATION
HYDROSIZER
HYDROSCILLATOR
SCREENS, DSM TYPE
FINES MINUS 35 PLUS 150-MESH
REAGENT CONDITIONER
PADDLE
REAGENT CONDITIONER
ROTARY
PADDLE
ROUGHER FLOTATION
10-AIRFLOW
7-SUB-A-DENVER
1-TURBO
1-AIR CELL
1-FAGERGREN
FROTH
TAILS
WASTE
TAILS
COARSE CONCENTRATION
5-BELT SEPARATORS
3-SHAKING TABLES
2-FLOTATION MACHINE
2-UNDERWATER SCREENS
1-SPIRAL
ACID
AGITATOR
DEOILING
SCREW CLASSIFIER
COARSE CONCENTRATE
SILICA FLOTATION
CONCENTRATE
FROTH
WASTE

FIGURE 39 GENERALIZED FLOWSHEET OF A FLOTATION PLANT FOR RECOVERING FLORIDA PHOSPHATE

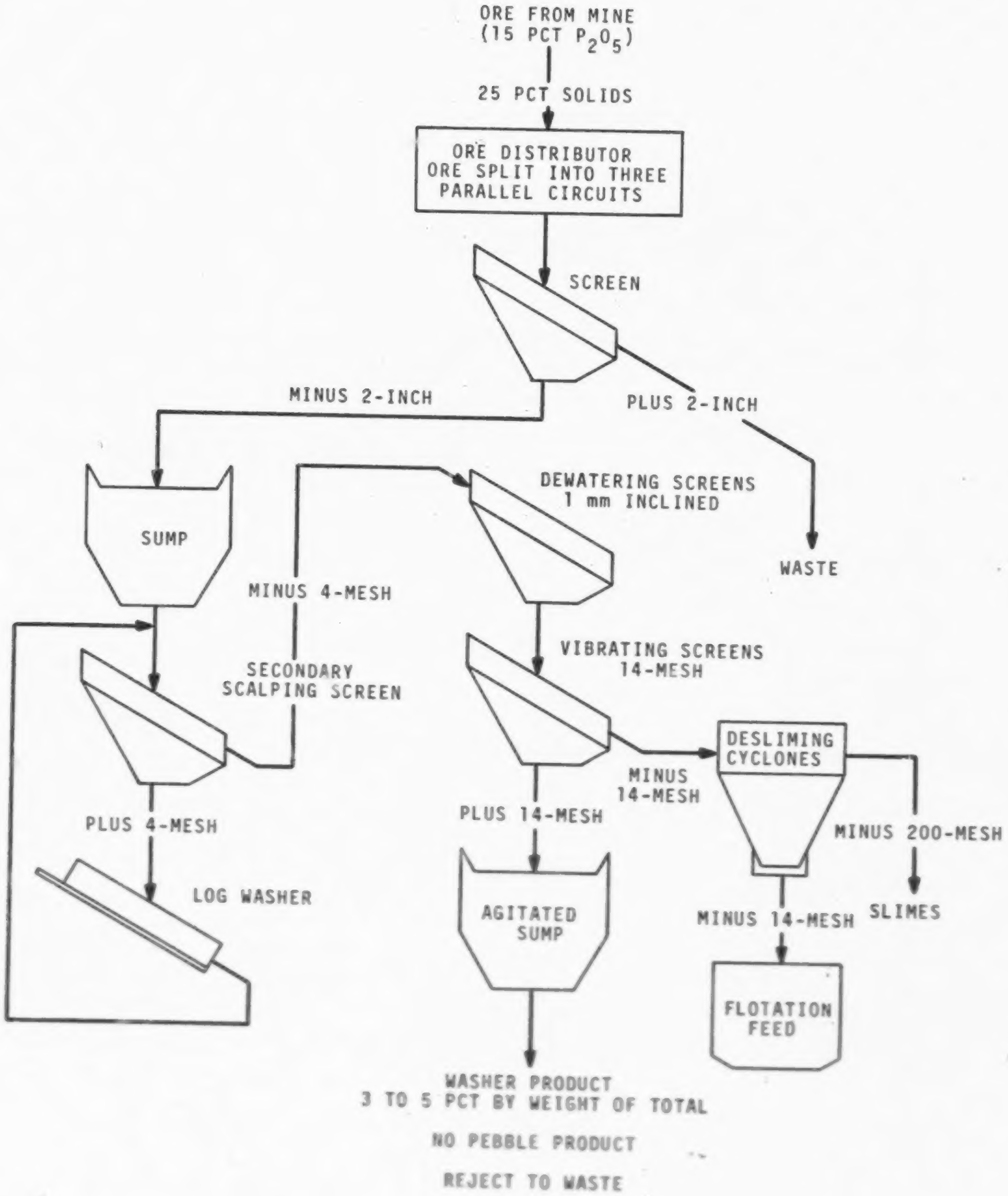

ORE FROM MINE
(15 PCT P2O5)
25 PCT SOLIDS
ORE DISTRIBUTOR
ORE SPLIT INTO THREE
PARALLEL CIRCUITS
SCREEN
MINUS 2-INCH
PLUS 2-INCH
WASTE
SUMP
DEWATERING SCREENS
1 mm INCLINED
MINUS 4-MESH
SECONDARY
SCALPING SCREEN
VIBRATING SCREENS
14-MESH
DESLIMING
CYCLONES
MINUS
14-MESH
PLUS 4-MESH
PLUS 14-MESH
MINUS 200-MESH
LOG WASHER
AGITATED
SUMP
MINUS 14-MESH
SLIMES
FLOTATION
FEED
WASHER PRODUCT
3 TO 5 PCT BY WEIGHT OF TOTAL
NO PEBBLE PRODUCT
REJECT TO WASTE

FIGURE 40 GENERALIZED FLOWSHEET OF A WASHER PLANT FOR RECOVERING NORTH CAROLINA PHOSPHATE

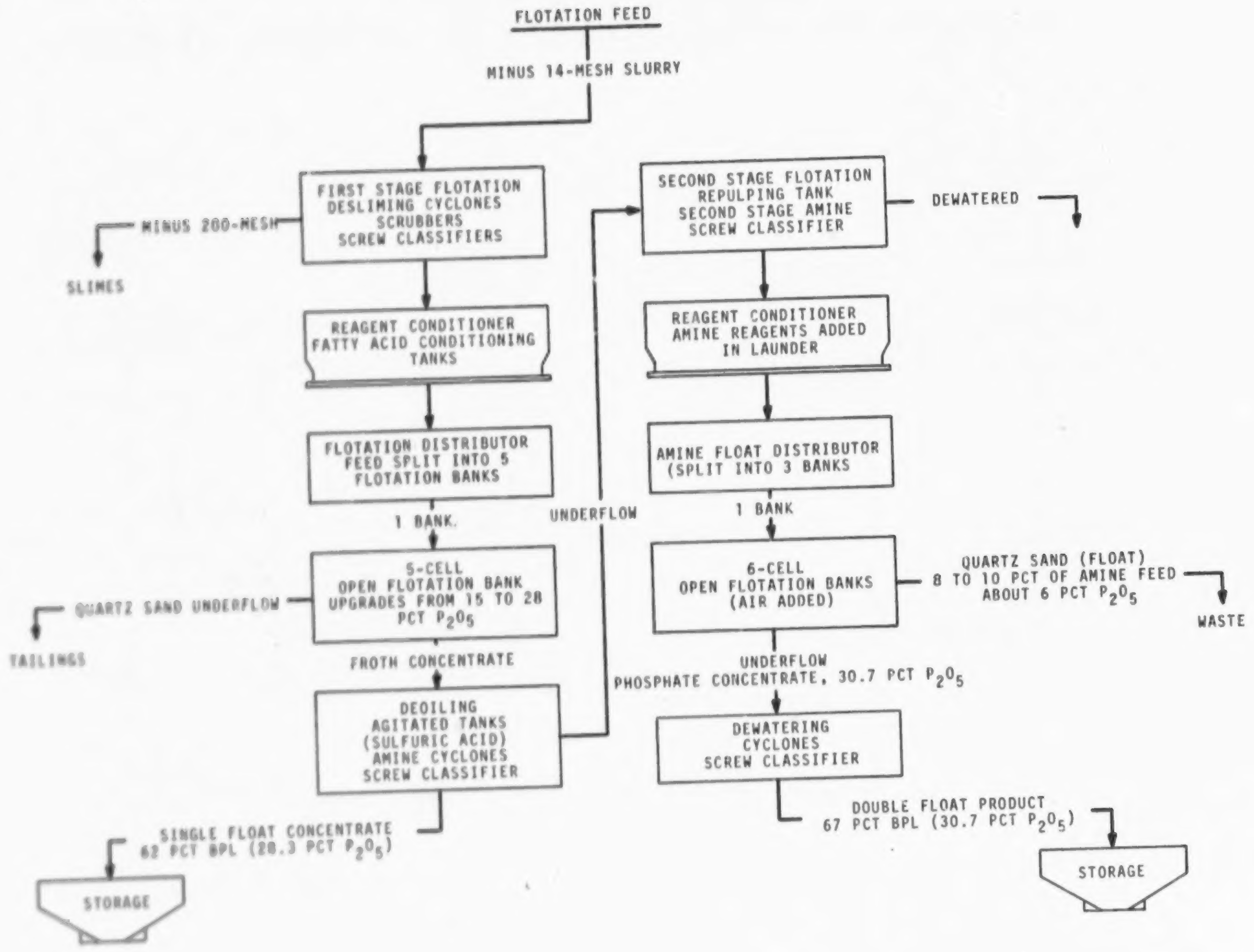

FLOTATION FEED
MINUS 14-MESH SLURRY
FIRST STAGE FLOTATION DESLIMING CYCLONES SCRUBBERS SCREW CLASSIFIERS
MINUS 200-MESH
SLIMES
REAGENT CONDITIONER FATTY ACID CONDITIONING TANKS
FLOTATION DISTRIBUTOR FEED SPLIT INTO 5 FLOTATION BANKS
1 BANK.
5-CELL OPEN FLOTATION BANK UPGRADES FROM 15 TO 28 PCT P_2O_5
QUARTZ SAND UNDERFLOW
TAILINGS
FROTH CONCENTRATE
DEOILING AGITATED TANKS (SULFURIC ACID) AMINE CYCLONES SCREW CLASSIFIER
SINGLE FLOAT CONCENTRATE 62 PCT BPL (28.3 PCT P_2O_5)
STORAGE
UNDERFLOW
SECOND STAGE FLOTATION REPULPING TANK SECOND STAGE AMINE SCREW CLASSIFIER
DEWATERED
REAGENT CONDITIONER AMINE REAGENTS ADDED IN LAUNDER
AMINE FLOAT DISTRIBUTOR (SPLIT INTO 3 BANKS
1 BANK
6-CELL OPEN FLOTATION BANKS (AIR ADDED)
QUARTZ SAND (FLOAT) 8 TO 10 PCT OF AMINE FEED ABOUT 6 PCT P_2O_5
WASTE
UNDERFLOW PHOSPHATE CONCENTRATE, 30.7 PCT P_2O_5
DEWATERING CYCLONES SCREW CLASSIFIER
DOUBLE FLOAT PRODUCT 67 PCT BPL (30.7 PCT P_2O_5)
STORAGE

FIGURE 41 GENERALIZED FLOWSHEET OF A FLOTATION PLANT FOR RECOVERING NORTH CAROLINA PHOSPHATE

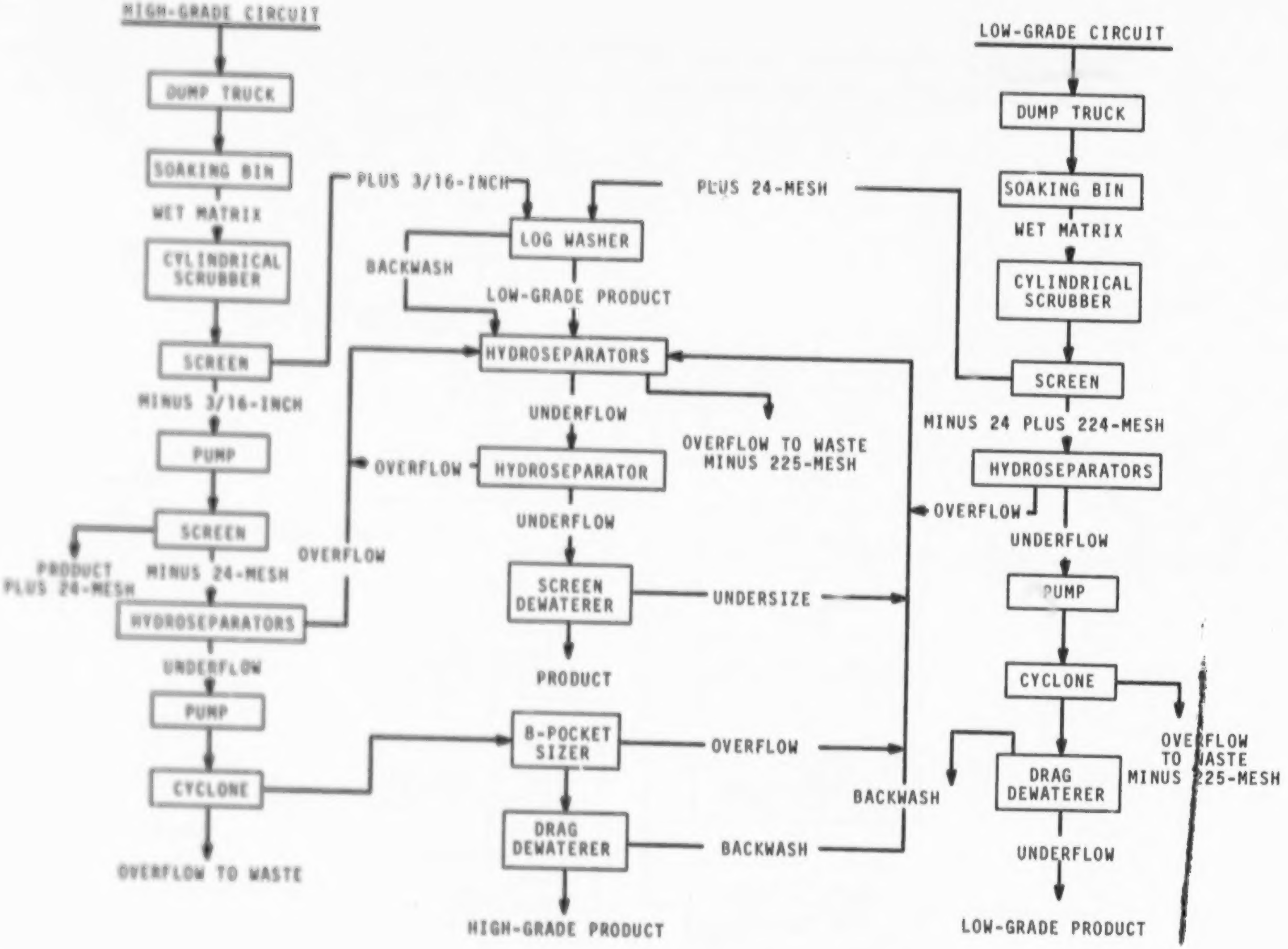

HIGH-GRADE CIRCUIT
DUMP TRUCK
SOAKING BIN
WET MATRIX
CYLINDRICAL SCRUBBER
SCREEN
MINUS 3/16-INCH
PUMP
SCREEN
PRODUCT PLUS 24-MESH
MINUS 24-MESH
HYDROSEPARATORS
UNDERFLOW
PUMP
CYCLONE
OVERFLOW TO WASTE
PLUS 3/16-INCH
PLUS 24-MESH
LOG WASHER
BACKWASH
LOW-GRADE PRODUCT
HYDROSEPARATORS
UNDERFLOW
OVERFLOW TO WASTE MINUS 225-MESH
OVERFLOW
HYDROSEPARATOR
OVERFLOW
UNDERFLOW
SCREEN DEWATERER
UNDERSIZE
PRODUCT
B-POCKET SIZER
OVERFLOW
DRAG DEWATERER
BACKWASH
HIGH-GRADE PRODUCT
LOW-GRADE CIRCUIT
DUMP TRUCK
SOAKING BIN
WET MATRIX
CYLINDRICAL SCRUBBER
SCREEN
MINUS 24 PLUS 224-MESH
HYDROSEPARATORS
OVERFLOW
UNDERFLOW
PUMP
CYCLONE
OVERFLOW TO WASTE MINUS 225-MESH
DRAG DEWATERER
BACKWASH
UNDERFLOW
LOW-GRADE PRODUCT

FIGURE 42 FLOWSHEET OF A WASHING PLANT FOR TENNESSEE BROWN ROCK PHOSPHATE

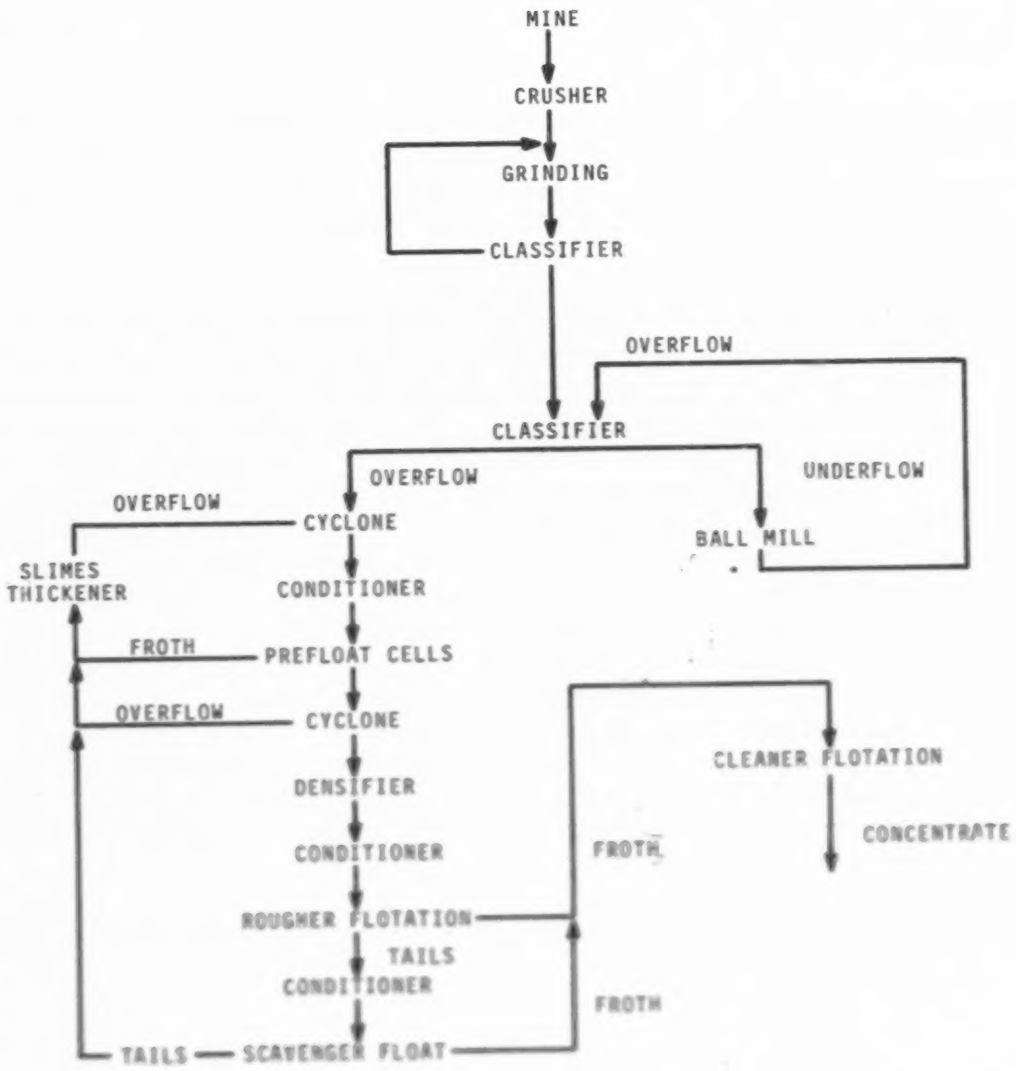

MINE
CRUSHER
GRINDING
CLASSIFIER
OVERFLOW
CLASSIFIER
OVERFLOW
UNDERFLOW
OVERFLOW
CYCLONE
BALL MILL
SLIMES THICKENER
CONDITIONER
FROTH
PREFLOAT CELLS
OVERFLOW
CYCLONE
CLEANER FLOTATION
DENSIFIER
CONCENTRATE
CONDITIONER
FROTH
ROUGHER FLOTATION
TAILS
CONDITIONER
FROTH
TAILS
SCAVENGER FLOAT

FIGURE 43 TYPICAL FLOWSHEET OF A WESTERN PHOSPHATE ROCK OPERATION

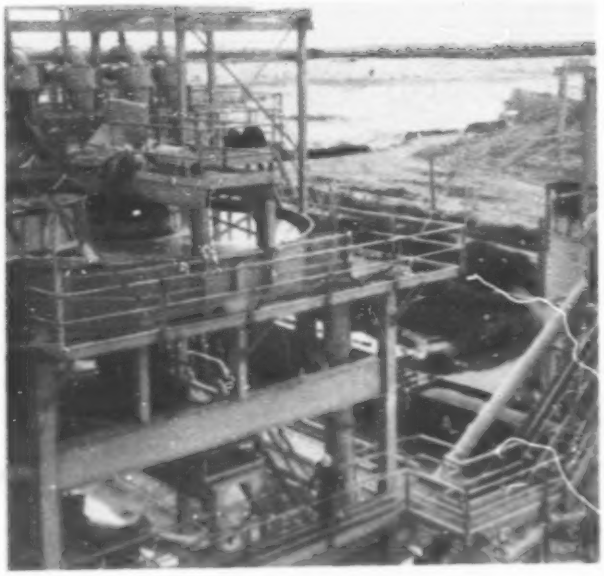
treatment by flotation. The flotation process yields a silica tail, a coarse concentrate, a fine concentrate, and a low-grade phosphate waste product.

In the washer, the main concern is to break up the lumps of clay to free the phosphate nodules. This is usually accomplished by a hammermill or similar apparatus, except in the Western operations where grinding mills are used. The nodules themselves are attrition-scrubbed in the log washers to remove adhering clay particles from the phosphate nodules. The washer rock is generally a little lower in phosphate content than the flotation concentrates. Figure 44 shows views of a typical Florida washer plant.

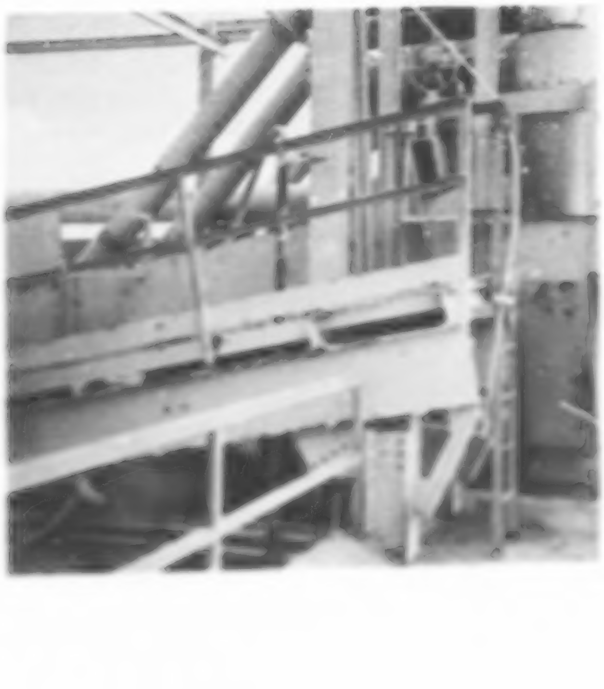
In the flotation plant feed preparation section, the size split for flotation plant feed is made by cyclones, rake classifiers, spirals, or hydroseparators. In general, this size split varies between 20 to 35 mesh with the fine fraction being sent to flotation.

The size fraction 14 by 35 mesh is then concentrated by several methods such as spirals, tables, belt separators, and coarse flotation. The minus 35 plus 150 mesh fraction is dewatered to approximately 60 percent solids, then placed in vertical agitated conditioning tanks. Reagents of the fatty acid type are added to the conditioning tanks to allow the flotation reagent to coat the mineral particles. The conditioned pulp is then floated in the rougher flotation section with the tailings going directly to the disposal area. The concentrate (froth product) is then put into a conditioning tank with sulfuric acid to remove the reagents added in the rougher flotation step. The concentrate is then washed. The cleaned and washed concentrate is then reagentized with an amine to float the silica away from the phosphate. The silica product thus floated is then discarded, while the fraction that did not float is dewatered and sent to storage as a phosphate rock concentrate.

The generalized reagent consumptions are given in Table 20.



Washer plant showing cyclones and hydroclassifier



Washer plant showing the cyclones and rake classifier

FIGURE 44 VIEWS OF A TYPICAL FLORIDA WASHER PLANT

TABLE 20

GENERALIZED REAGENT CONSUMPTION IN CONCENTRATING PHOSPHATE BY FLOTATION(7)

(Pounds per ton of ore)

Fatty Acid Flotation Step
- NaOH - 0.3 to 1.5
- Fatty Acids - 0.75 to 1.25
- Fuel Oil - 1 to 3

Cleaning Step
- H_2SO_4 - 0.5 to 3.0

Amine Flotation Step
- NaOH - 0.1 to 0.3
- Amine - 0.1 to 0.3
- Kerosene - 0.0 to 0.50

In general, reagent consumption is determined by how well the flotation feed has been deslimed and the extent of conditioning of the mineral surfaces.

The plant output to wet storage is analyzed for size, BPL, Na, K, F, and As. The products are stored by BPL content and size. Some of the product is ground as a customer service and some lower-grade material is blended to meet shipping specifications. The common shipping grades in percent BPL are 68, 72, 75, and 77. A small percentage of the phosphate concentrate is calcined to remove organic material for use in the production of furnace acid.

EFFLUENTS FROM MINING AND BENEFICIATION

The effluents produced in the mining and beneficiation of phosphate rock are contained in the water suspensions leaving the washer plant. These suspensions are the phosphate slimes and the sands tailings. The amounts of these effluents relative to the water balance and water flow rates for a typical Florida plant operation processing 36,000 tons per calendar day of phosphate matrix (approximately 6000 tons P_2O_5 per day) is given in Table 21. The flows presented correspond to a water usage of about 13 gallons per minute per daily ton of P_2O_5 production assuming a phosphate matrix containing about 16.5% P_2O_5.

TABLE 21

WATER DISTRIBUTION FOR A TYPICAL FLORIDA PLANT OPERATION(8)

	Gallons Per Minute	Percent of Total Water Used
Source for Water Used		
Reclaimed from all ponds	57,200	74
Water from deep wells	20,000	26
TOTAL	77,200	100
Estimated Water Usage		
Mining (matrix)	10,000	13
Processing	22,000	28
Slimes disposal	39,000	51
Sand tailings	6,200	8
TOTAL	77,200	100

It can be noted that the major effluent is that of the slimes which contain a suspension of clays and very fine solids amounting to about 4 to 6 percent by weight of the slimes stream. A typical analysis of these slime solids is provided in Table 22.

As previously noted, these slimes are impounded in slimes ponds to allow settling and clarification to occur. Clear water is returned from the ponds to the beneficiation plant. Figures 45 and 46 show views of slime ponds and water drainage for recycle to the beneficiation plant.

TABLE 22

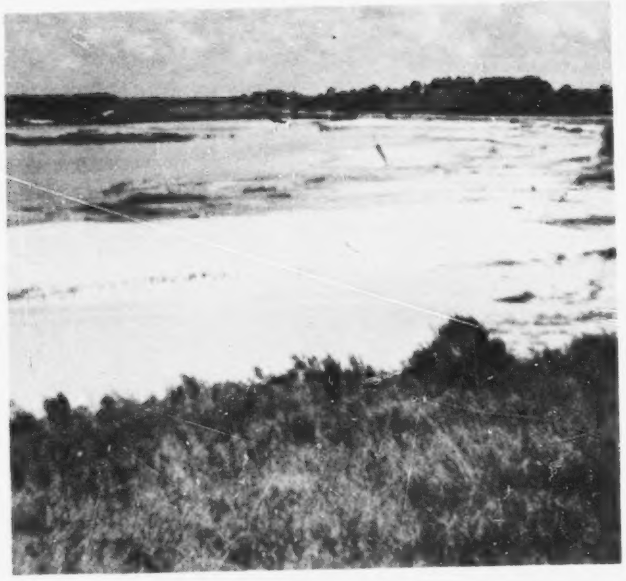
APPROXIMATE MINERALOGIC AND CHEMICAL COMPOSITION OF PHOSPHATE SLIME SOLIDS (8)

Approximate Mineralogical Weight Composition of Phosphate Slimes Solids

Mineral	Percent
Carbonate fluorapatite	20 - 25
Quartz	30 - 35
Montmorillonite	20 - 25
Attapulgite	5 - 10
Wavellite	4 - 6
Feldspar	2 - 3
Heavy minerals	2 - 3
Dolomite	1 - 2
Miscellaneous	0 - 1

Chemical Composition of Phosphate Slimes Solids

Chemical	Typical Analyses, percent	Range, percent
P_2O_5	9.06	9 - 17
SiO_2	45.68	31 - 46
Fe_2O_3	3.98	3 - 7
Al_2O_3	8.51	6 - 18
CaO	14.00	14 - 23
MgO	1.13	1 - 2
CO_2	0.80	0 - 1
F	0.87	0 - 1
LOI (1,000 C)	10.60	9 - 16
BPL	19.88	19 - 37



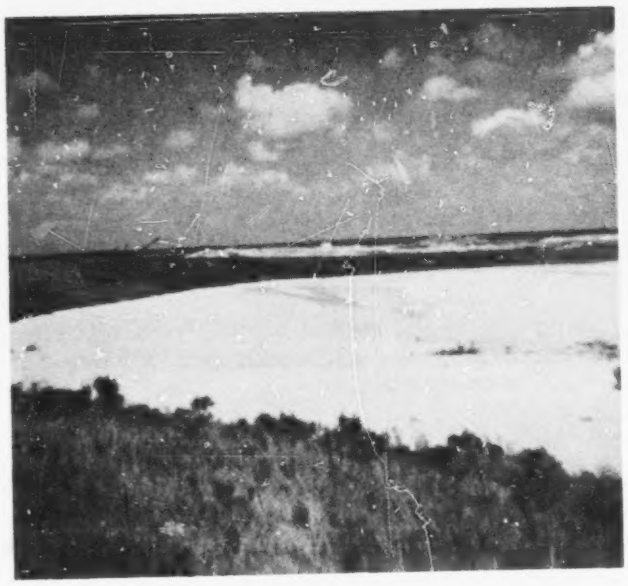


FIGURE 45 VIEWS OF FLORIDA SLIME PONDS AND DIKES

FIGURE 46 VIEW OF WATER DRAINAGE FROM SLIME PONDS FOR RECIRCULATION TO PLANT

ENVIRONMENTAL AND POLLUTION EFFECTS OF EFFLUENTS FROM MINING AND BENEFICIATION

The environmental effects of the aqueous effluents from phosphate mining and beneficiation were investigated by R. C. Specht in 1947 in relation to the waste disposal practices of the Florida phosphate companies. The investigation was conducted along the river basins of the Peace and Alafia Rivers. Extensive sampling was conducted and numerous tests were made to determine the amount or effect of:

1. Turbidity
2. Dissolved oxygen and biochemical oxygen demand
3. Alkalinity
4. Toxicity of flotation chemicals.

The turbidity of the stream waters was found to increase by about 2.5 percent as a result of process effluents; however, tests with fish of several varieties showed no effect on fish life. The effect of turbidity on plankton growth was not investigated.

The dissolved oxygen (DO) and biochemical oxygen demand (BOD) analyses indicated that the dissolved oxygen content of the stream was increased and thereby improved, and the biochemical oxygen demand was not changed significantly by the phosphate operation effluents.

No change in alkalinity of the receiving streams was detected except in one case where the effluents were beneficial in neutralizing trace acidity in the stream.

The only chemical used in the operation that could be toxic at existing concentrations was tall oil; however, no tall oil was found in the effluent waters. The tall oil is used to coat the phosphate mineral to promote flotation, and tends to go with the phosphate concentrate. However, any residual tall oil will tend to be precipitated by the calcium in the streams. The kerosene, acids, amines, and caustic did not appear in sufficient amount to be toxic to the fish tested. The conclusion of the Specht study was that aside from an apparent increase in algae growth, the effluents from the phosphate operations are not harmful to the environment.

Figure 47 shows a view of plant growth in an old slime pond.

One fact that should be noted here is that because of the large water consumption necessary in phosphate operations this water usage might lower the water table, thereby causing contamination of the aquifer. One such case has been recorded; however, available details are insufficient to draw any conclusions.(43,44)

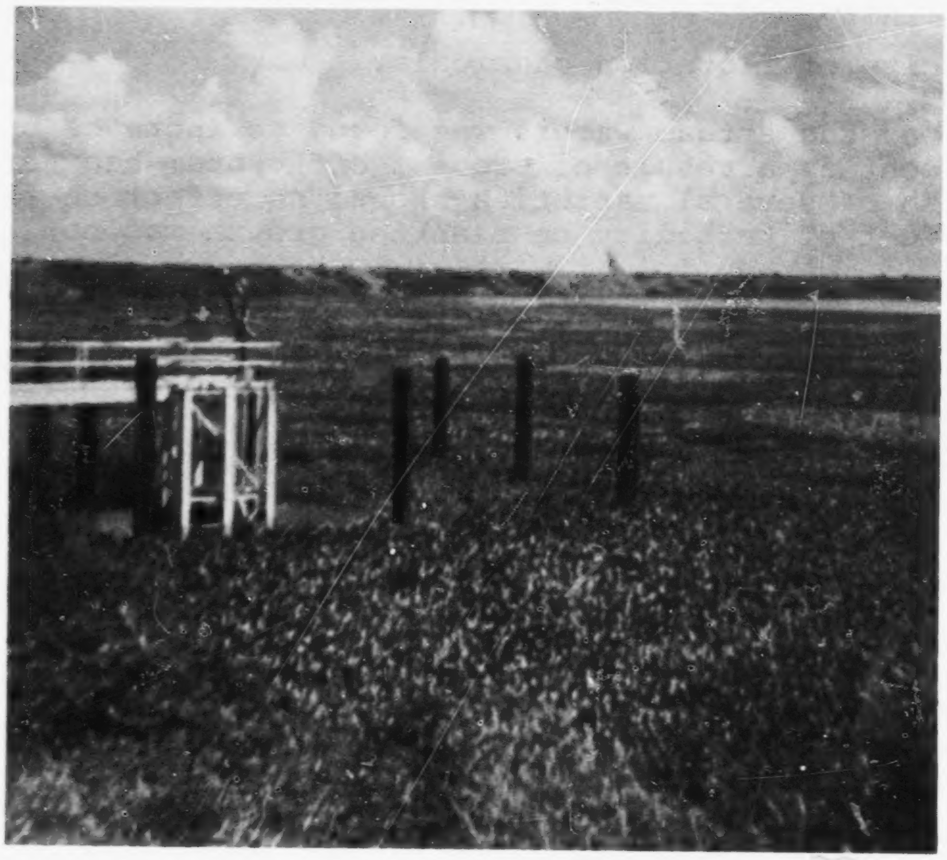


FIGURE 47 VIEW OF A SLIME POND SHOWING GROWTH OF WATER PLANTS

CONTROL AND TREATMENT OF AQUEOUS EFFLUENTS

The aqueous effluents from mining and beneficiation of phosphate rock are presently controlled by the use of large settling ponds. The slimes are allowed to settle and the clear water is drawn off and returned to the plant for reuse. The slime ponds are built to rigid specifications and surveillance of the pond areas is maintained.(8) The restrictions concerning pond construction in Florida are enforced by both the state and phosphate mining companies. The effectiveness of present effluent control practices is good. There has been no major slime pond failure for the last 3 years.

Means to significantly improve effluent control are not apparent from the result of work to date. Considerable research has been conducted by the Bureau of Mines, TVA, and the individual companies on the beneficiation or dewatering of the slimes and possible uses for the slime solids. This work has not led to practical results. At present, only a minor amount of basic research is being conducted on means to alleviate the slimes disposal problem. Most of the research being conducted is on variations in the physical handling of the slimes to reduce costs and water losses.

An example of work currently being performed in the industry is the program at American Cyanamid Company's Brewster Plant.(10) American Cyanamid conducted tests for several months, trying to determine a simple economical way of reducing the water content of the slimes and the volume they occupied. A trench was dug that was 5,000 feet in length, 136 feet wide, and 35 feet deep.(11) The slimes were poured into the trench and allowed to settle to a density of approximately 25 percent solids. Sand was then poured into the trench, and within a few hours water was noted to be forced to the surface. This water was drained off, leaving the resulting mixture approximately 80 to 90 percent solids. American Cyanamid found that the volume occupied by the sand and slime mixture was the same or less than the volume occupied by the slimes. This method of slime disposal reduces the slime handling costs by approximately one-third and returns the land to useful purposes. Photographs showing two views of this operation are shown in Figure 48. This procedure appears to provide a definite improvement in handling a part of the slimes; however, this approach is only a partial answer because the amount of slime that is generated is greater than the amount of sand tails normally produced in the mining operation.

The general practice of the Florida phosphate companies is to monitor the streams below their plants for water flow, suspended solids, phosphate, and fluorine. These streams

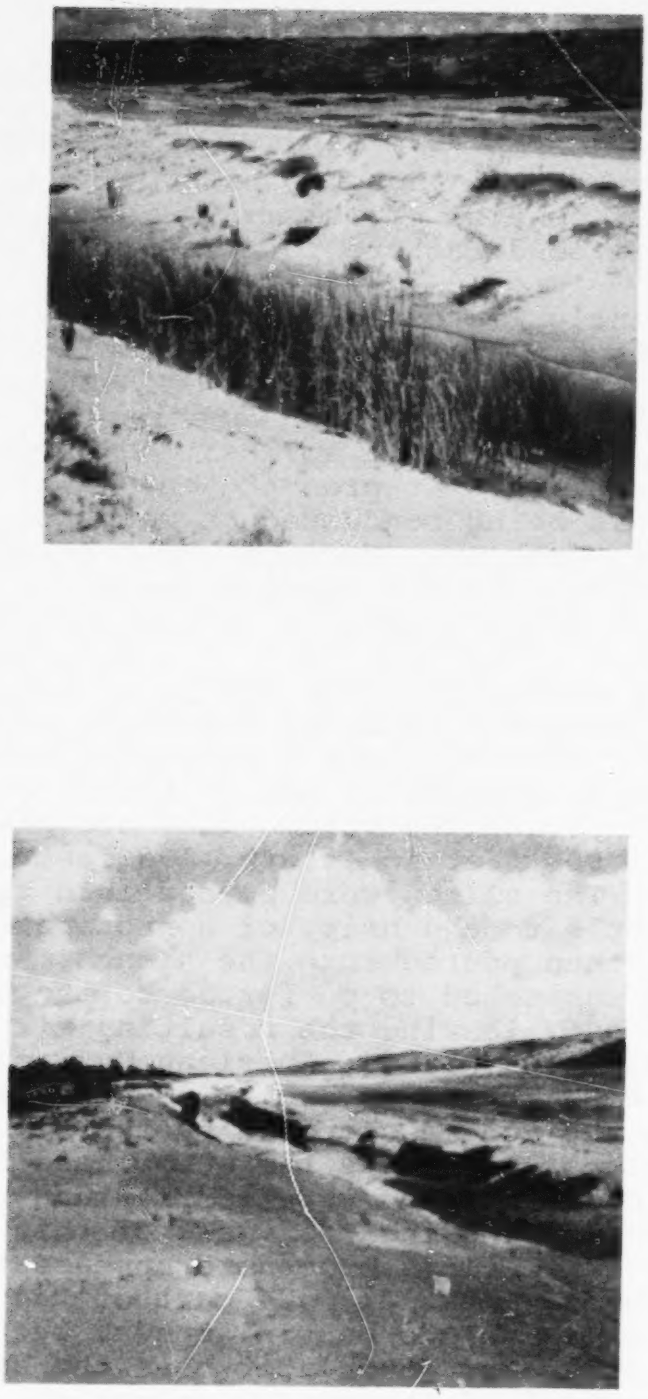


FIGURE 48 VIEWS OF AMERICAN CYANAMID'S NEW STAGE-FILLING TECHNIQUE FOR SLIME DISPOSAL

are checked on a daily basis so that any rise above normal in any one of the measured variables can be quickly detected and the source traced down. New methods to continuously monitor these variables are now being studied, including specific ion electrodes, direct reading spectrographs, chemiluminescence and conductivity.

ECONOMIC ASPECTS OF EFFLUENT CONTROL

Control of the primary effluent from the phosphate rock mining and beneficiation is accomplished by building and maintaining the slime ponds. A significant portion of the total operating costs is related to this part of the operation. Table 23 gives a breakdown of the estimated total capital and operating costs for a typical slime disposal system.(8) It is evident from Table 23 that, to be of significant near-term interest to present operators, any new procedure for slimes and tailings disposal must be accomplished at costs not greatly exceeding $0.25 per ton of phosphate rock product or about $0.50 per ton of dry slime solids.

TECHNICAL ASPECTS OF IMPROVED EFFLUENT CONTROL

It is significant that approximately one-third of all phosphate value mined is now lost in the slimes. Currently, the slimes produced annually from the Florida operations contain more phosphate than was produced as salable product in 1960. The magnitude and severity of the slimes problem in Florida can be estimated from the fact that almost 500,000,000 gallons of water per day are associated with the rejected phosphate slimes.

The reason this waste continues is that, despite substantial study, a low-cost method to dewater phosphate slimes has not been developed. As previously noted, it is estimated that disposal in ponds costs about $0.25 per ton of contained solids. This is less than $0.10 per 1,000 gallons of water contained. The characteristics of the slimes make them extremely difficult to process and there is no method for dewatering proposed to date that has shown significant promise or has been developed sufficiently to meet present economic limitations.

The problem is technically difficult because the solid particles are almost all of colloidal size and extremely hydrophilic. The solids are extremely slow to settle. Even after years of settling, the solids content of the slime ponds does not exceed 30 weight percent. At 30 percent solids, the phosphate slimes are almost of jelly-like consistency. Centrifuging produces material containing only 35 percent solids.

TABLE 23

CAPITAL AND OPERATING COSTS FOR SLIMES DISPOSAL(8)

Capital Costs

	Capital Investment
Slime pump stations (3 complete units)	$700,000
Pond spillways (10 required)	80,000
Excavator (for ditching)	60,000
Pumps (4 recirculating water)	160,000
Pipeline	200,000
Plant facilities	72,000
Plant utilities	76,000
Total cost (tax and insurance base)	$1,348,000
Interest during construction	33,700
Subtotal (depreciation)	1,381,700
Working Capital	280,200
Total capital investment	$1,661,900

Operating Costs

	Unit cost	Total	Cost per ton of product[1]
Direct cost:			
Raw materials and utilities:			
Fuel - 13.3 gal x $0.15 x 40 hr x 52 weeks	$4,100		
Power - 2,150 kwhr/hr x 8,760 hr/yr x $0.01 kwhr	188,300		
		$192,400	$0.045
Direct labor:			
16 man-hr/day - $3.00/man-hr x 365 day/yr	17,500		
Supervision - 15 percent of labor	2,600		
		20,100	.005
Maintenance:			
5 men - $7,000/yr	35,000		
Supervision - 20 percent of maintenance labor	7,000		
Material -	17,500		
		59,500	.014
Payroll overhead - 25 percent of payroll		15,500	.004
Operating supplies - 20 percent of maintenance		11,900	.003
Total direct cost		299,400	.071
Indirect Cost:			
40 percent of labor, maintenance, & supplies		36,600	.009
Fixed Cost:			
Taxes and insurance - 3 percent of total cost		40,400	.010
Depreciation - 5 percent of subtotal for depreciation and 10 percent for excavator		72,100	.017
Dam construction		938,000	.223
Total operating cost		1,386,500	.330
Credit for recirculated water		358,100	.085
Net operating cost		$1,028,400	.245

---

[1] Cost per ton is based on 4,205,000 tons of product.

The most immediate need is to develop means to dewater the slime economically. Although the slimes contain substantial phosphate values that might be recovered, utilization of slimes will probably depend on initial dewatering. Even if the phosphate values could be recovered today by selective removal from the slimes, disposal of the remaining slimes would still be a major problem that must be resolved by means other than the slime pond.

A discussion of the technology of treating the phosphate slimes is not meaningful without considering the economics. One consideration is that utilization of contained phosphate value would almost certainly require drying. It is estimated that drying fuel costs alone would be at least $3-4 per ton of dry 30 percent P_2O_5 material. Considerably higher costs would be incurred if multiple-effect evaporation could not be employed. Actually, it is doubtful that the slimes could be dried for less than $8 per ton equivalent to 30 percent P_2O_5 material. Moreover, the P_2O_5 content of the slime is less than half that of the rock being sold, and some means to upgrade to over 30 percent P_2O_5 would be required. Florida phosphate can be produced for considerably less than this estimated drying cost. In view of the availability of lower grade Florida and Western phosphates that would be an economically more favorable source of P_2O_5 than the slimes, there appears to be virtually no possibility that the P_2O_5 can be economically recovered from the slimes.

Thus, the phosphate slimes problem is really a problem in disposal. It has been estimated that the cost of slime pond disposal in Florida is about $0.25 per ton of contained solids or about $0.10 per 1,000 gallons of slime. Therefore, for an alternate method to be of near term interest, it must offer the possibility of dewatering at costs well below about $0.50 per ton of solids or $0.10 per 1,000 gallons of contained water.

Experience in prior related investigations suggests that no single process step can offer optimum processing. A combination of steps would probably be most economical for the range of concentration of interest.

REVIEW OF PRIOR RESEARCH RELATED TO PHOSPHATE SLIMES DISPOSAL

The Tennessee Valley Authority worked for many years on various methods of partial dewatering of slimes. Appendix A provides an outline of their work. Although no economic method of dewatering was found, three methods were encouraging, viz.:

1. Thickening with slow stirring (to 30 percent solids)
2. Freezing (solids settled rapidly to 45 percent, filtered rapidly to 60 percent)
3. Electrophoresis (to 50 percent solids).

The United States Bureau of Mines did extensive research on combined dewatering and recovery of phosphate and/or other values from the slimes by physical beneficiation or chemical extraction.(12) Appendix B outlines the scope of their program. The work by Stanczyk, et.al., on dewatering by combination of electro-osmosis and vacuum filtration(13) is also significant.

In a pilot plant run on electrical dewatering of phosphate tailing, Houston, et.al.,(14) report power consumption of 65 kwhr per ton of solids removed, with a deposition rate of 8 lb per sq ft per hour. A rotating drum type of continuous dewatering machine with a cast iron anode was used. The process is not yet competitive with the use of settling pond.

Elaborate work by Thompson(15) and later by Thompson and Vilbrant(16) on use of ultrasonic energy for coagulation and settling of solids in phosphate tailing illustrates the range of concepts tried for a solution of the problem. Near the isoelectric point, mild intensity (below caviation level of 0.3 volt-ampere per sq cm) insonation increased the coagulation and subsequent settling rate by a factor of 5 as compared to a control without ultrasonic energy. Intense insonation above certain limits had the opposite effect, increasing the thixotropic gel structure and, consequently, retarded settling. Studies by Sun and Smit(17) on flotation reclamation of phosphate from slime produced some interesting results. Phosphate flotation of Bartow washer slime by fatty acid (Pamak-1) was improved by classification at 10.0, 5.0, 2.5, and 1.25 microns. Flotation effectiveness was approximately proportional to size. As would be expected, the flotation efficiency decreased drastically for particles under 5-micron size.

The elegant analysis by Derjaguin and Dukhin(18) on the mechanics of fine-particle flotation reveals some of the difficulties involved in colloid flotation.

Studies by Greene and Duke(19) on selective flotation of ultrafines as applied to both the Florida and Tennessee phosphatic slime demonstrated some practical possibilities. Addition of extraneous material like sulfur as a carrier improved flotation of phosphates from the Florida slime. Tennessee slime did not respond to such treatment when sulfur was used as the carrier.

A recent patent by the same authors(20) describes a process for tumbling phosphate slimes with 10-35 mesh angular silica sand for several hours and then floating the pulp after removing silica sands by screening. The process shows significant improvement in flotation of phosphate fines (>9 microns). A 30 percent increase in recovery of phosphate (85.4 percent recovery) was demonstrated in comparison with operations without the sand tumbling.

Haseman's(21) proposal of selective flocculation of colloidal phosphate with starch created considerable interest which resulted in more intensive study of flocculation, subsidence and filtration of phosphate slimes by La Mer, et.al.(22-27) They have noted significant improvement in filtration by addition of potato starch. Appendix C shows comparative results for the 12 most promising flocculant gums and polyelectrolytes in a group of 150 tested. Dow Chemical's "Separan 2610" showed the best results. Theoretically, it seems highly doubtful that dewatering with hydrophilic sols would succeed beyond 20-30 percent solids.

Mellgren and Shergold(28) describe a method for recovering ultrafine mineral particles by extraction with an organic phase. By using a suitable surfactant, the contact angle of the solids in the liquid phase can be modified to let the mineral particles concentrate either at the liquid-liquid interface or in the organic phase. Tests by Shulman and Lejas(29) on an emulsion stabilized by barium sulfate confirm the feasibility of the principle.

Takauwa and Takamori(30) have investigated the possibility of a phase inversion technique for quick appraisal of laboratory flotation results. Agglomeration of fine solids in liquid suspension by preferentially wetting the solids with another liquid which acts as a bridging agent between the particles has been the subject of a patent.(31) The technique was further elaborated in a paper by Fernand, et.al.(32)

Of significance to the problem of colloid flotation of phosphatic slime are works by Clanton,(33) Magoffin and Clanton,(34) and Grieves, et.al.(35-41)

Clanton and co-worker's attempts were directed mainly at the removal of sols from textile wastes. Ferric oxide sols were floated with kerosene sodium oleate combination to almost 100 percent removal. Similar tests were unsuccessful in floating chromium oxide sols.

Grieves, et.al.'s work centered on removal of surfactants from liquids by foam fractionation. While studying the effect of suspended material on foam separation of anionic and cationic surfactants,(37) they observed that colloidal particles could be removed along with the foam. Using this principle, they removed ferric hydroxide sols with dodecalsodium sulfate.(38) The volume of foam removed was a significant weight fraction of the original mass, but the recovery of the colloids was not sufficient to produce fully clarified water.

RECOMMENDATIONS FOR RESEARCH TO DEVELOP IMPROVED MEANS FOR DISPOSAL OF EFFLUENTS FROM PHOSPHATE MINING AND BENEFICIATION

It is recommended that research be undertaken to better establish the merits and technical-economic limitations of various methods known to provide some basis for successful development of an improved slimes-disposal system. It is anticipated that, upon completion of the effort, the most profitable directions for emphasis on subsequent development programs would be known. Such work should result in the development of an economic dewatering process, through analysis of the slimes system and definition of the merits and limitations of processing known to be technically effective in slimes recovery and dewatering.

The promising process concepts that can be applied to concentrate and dewater the slimes can be classified as: (1) surface chemical, (2) electrochemical, (3) thermal, and (4) combinations of these. Comments follow concerning the background and research effort believed warranted within the classifications listed.

(1) Surface Chemical Research. In general, the lowest cost separation method will be based on physical separation. However, a limitation on physical separation in colloid suspension is dictated by surface chemistry factors. To better understand flocculation, filtration, and flotation processes, it will be necessary to know more about reagent adsorption on the slime components and capability to alter or eliminate the hydrophilic nature of the clays. A key focus for the work on surface chemistry should be to determine possibilities to reduce requirements for flocculant reagents by use of selective adsorption on the surface of components present in the slimes in only minor amounts or by selective adsorption on only certain types of adsorption sites. A practical objective would be to achieve satisfactory flocculation using 1-2 parts per million (ppm) quantities of flocculants rather than the 100-200 ppm range required for flocculation with polyacrylamides and potato starches.

It was noted in preliminary experiments recently made at Battelle that chelating agents can be used to render the slimes hydrophobic, and thus floatable. The amount of reagent required, from a practical standpoint, was excessive in these experiments.

However, the possibility that certain metal ion sites can be chelated selectively with trace quantities of agents which can bridge to a flotation collector deserves attention as a possible method to reduce reagent requirements for initial partial dewatering by bulk colloid flotation or selective separation.

In summary, the required activity for surface chemistry research is to study adsorption of reagents which promote flocculation and/or alter the hydrophilic nature of the slimes solids. The objective of this work would be to better understand factors influencing the minimum reagent requirements.

(2) Electrochemical Research. Application of an electric field to a suspension of fine particles causes directional particle migration. Solids could thus be removed from suspension, either in bulk or perhaps selectively. This technology is termed electrophoresis. It is also possible to electrochemically dewater a suspension by causing movement of the medium (water) through a membrane by force of an electrical field (electro-osmosis).

Electrophoresis: Houston, et.al.(14) reported thickening of Tennessee phosphate slimes from 12.5 to 50 percent solid content by electrophoresis. The overall cost of dewatering Tennessee phosphate slimes by electrophoresis was estimated in 1952 by Tyler and Waggaman to be $2 per ton of dry slime versus $1 per ton for pond disposal. Since that time the technology on electrophoresis has advanced and the costs can probably be reduced substantially.

Work has shown that when surface properties of these "slimes" are modified (for example, by addition of a dispersant such as sodium silicate) the efficiency of electrophoresis increases. Superimposition of vacuum filtration with drum-type electrophoretic apparatus enhances the efficiency of the operation and can reduce the operating cost.

However, there are no published data on the dewatering of Florida phosphate slimes by electrophoresis. Experiments to obtain basic data to enable determination of optimum operating conditions and process costs are, therefore, warranted.

Electro-Osmosis: An attractive feature of electro-osmosis is that virtually clear water can be obtained for immediate reuse. Stanczyk and Feld(13) of the U.S. Bureau of Mines compared dewatering of Bartow phosphate slimes by electro-osmosis, vacuum filtration, and a combination of the two processes. The power requirements for the combination were found to be less than for electro-osmosis alone, and a function of applied voltage and solids content. Under the conditions studied, the power requirement for increasing the slimes solids from 15 to 35 percent was equivalent to about 15 kwhr per ton of dry slime solids.

(3) Thermal Processing Freezing. It has been known for some time that simple freezing and thawing of phosphate slimes causes irreversible changes in hydration so that solids will settle rapidly and to a relatively high solids content without addition of flocculants. Experiments made at Battelle with fresh Bartow slime samples demonstrated fast settling to 36 percent solids from a slime with an initial solids content of 2.7 percent. Pressure filtration then yielded a cake of 43 percent solids.

The economics of a slimes dewatering process based on freezing at first seem prohibitive. However, recovery of fresh potable water by freeze-desalting of sea water has received extensive study. Published cost estimates predict, perhaps optimistically, costs for a 1-million-gallon-per-day freeze-desalting facility as $0.40 per 1,000 gallons.(42) A representative of the Office of Saline Water has stated that freezing appears to be the most economical desalting process up to capacities of about 1 million gallons per day.*

It should be recognized that in freeze-desalting there is a brine reject containing not more than about 7 percent salt. Thus, freeze-desalting must process almost twice the amount of water that is produced. This would not be the case for slimes processing. Also, a freeze-desalting process is a far more complex process than the simple freezing and melting required for slimes. With slime processing there would be no need for washing the ice to remove occluded brine. If the $0.40 per 1,000 gallon estimate can be achieved for desalting, it is anticipated that costs less than $0.20 per 1,000 gallons, or about $1.00 per ton of dry slime solids, are possible. It is noteworthy that large-scale operations have been installed in England for freeze-based dewatering of water filtration and sewage sludge.

Careful study of the economic potential of freeze-based dewatering applied to phosphate slimes appears warranted because it provides potential for increased water reuse (fatty acids and amines from flotation would be removed and water recycled to flotation without adverse effect) and use of the dewatered slime solids for light-weight aggregate.

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*Private communication.

COORDINATION OF RECOMMENDED RESEARCH

Through discussion with representatives of the producing companies and various government agencies, it is well recognized that efforts are presently being made that relate to resolution of this difficult technical-economic problem. In addition to the basic objectives of the industry to improve phosphate recovery, minimize water usage, and minimize the land requirements and land maintenance costs, there are factors involved pertinent to state and federal agencies concerned with land and water resource management, water pollution, and solids waste disposal. Knowledge already developed and current research in progress could provide meaningful information if there is a coordinated program intended to resolve the slimes problem. Such coordinated effort is considered by Battelle to be the best procedure, if not the only procedure, that can lead to a near-term resolution of the problem. Implementation of a coordinated research program is therefore recommended.

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APPENDIX A

OUTLINE OF VARIOUS BASIC PROCESSES AND VARIATIONS TRIED BY TVA FOR PARTIAL DEWATERING AND SETTLING OF SLIME

APPENDIX A

OUTLINE OF VARIOUS BASIC PROCESSES AND VARIATIONS TRIED BY TVA FOR PARTIAL DEWATERING AND SETTLING OF SLIME*

(After Tyler & Waggaman)

SEDIMENTATION

- Chemical treatments
    - Dispersants
    - Flocculants
    - Modifiers, designed to delay gel formation or to produce more compressible gel
    - Heteropolar organic compounds to render clay hydrophobic
    - Positively charged in organic sols--e.g., aluminum and ferric oxide sols
    - Dyes, selectively adsorbed by clay
    - Dissimilar metal powders, galvanic action
    - Agents for removing calcium ion from solution, by precipitation
- Physical Treatments
    - Ultrasonic irradiation
    - Freezing
    - Weighting with sand or fly ash
    - Dehydration, concentrated salt solutions, extraction with ehter
    - Evacuation, to remove dissolved gases
    - Magnetic field to promote settling
    - Heating matrix or treating with silicone prior to washing to prevent hydration of the clay

THICKENING, WITH SLOW STIRRING

- Rate of stirring
- Type of stirring element
- Presettling
- Chemical treatments

FILTRATION

- Filter aids
- Heat
- Chemical treatment

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CENTRIFUGING

- Chemical treatment

DRYING

- High temperature
- Ambient temperature
- Forcing compressed air through suspension

ELECTRICAL METHOD

- Electrophoresis, direct current
  - Electrode spacing
  - Voltage gradient
  - Intermittent current
  - Chemical treatment
- Electrophoresis combined with sedimentation
- Electrophoresis combined with filtration
- Alternating current
  - Voltage
  - Frequency
- Magnetically induced current, by flow of suspension through a magnetic field

APPENDIX B

OUTLINE OF DEWATERING, CHEMICAL, AND PHYSICAL BENEFICIATION OF FLORIDA PHOSPHATE SLIMES BY USBM

APPENDIX B

OUTLINE OF DEWATERING, CHEMICAL, AND PHYSICAL BENEFICIATION OF FLORIDA PHOSPHATE SLIMES BY USBM(5)

I. DEWATERING

(a) Slime Flocculation and Thickening: 29 flocculants were tested for static flocculation tests. The maximum settling over a 24-hour period was obtained with citric acid (to 10% solid).

(b) Pressure Filtration: Filtration tests carried out in the laboratory at pressures ranging from 10 to 50 psig and 2 to 40 pounds of filter aid (diatomite). Also temperature was varied from 30 to 165 °C.

(c) Extraction of organic material before filtering: Organic solvents like acetone, ethyl alcohol, ethelyene glycol, 2,3,4-trimethyl pentane, and carbon tetrachloride were used as extractant for organic materials believed to be deleterious for filtration. Filtration rate did not show any improvement.

II. PHYSICAL BENEFICIATION

(a) Selective Oiling: Kerosene in combination with fatty acid collector were mixed with the slime and allowed to settle.

(b) Selective Flocculation: Haseman's(21) technique were investigated.

(c) Flotation: The froths obtained were easy to handle and flotation was rapid. Consumption of reagents were high.

(d) Cyclone Sizing: Phosphate distribution in various size fraction did not show any particular pattern of interest.

III. HYDROMETALLURGICAL BENEFICIATION

(a) Ion Exchange: Anonic resin. 5% extraction 70 hours contact time at pH 6 to 7.

(b) Acid Leach: Sulfuric, hydrochloric and nitric acids were tried. Phosphorus extraction similar by the three acids (1 lb acid per lb of slime dry basis: Extraction 82-96% phosphate).

IV **BACTERIOLOGICAL STUDIES**

(a) Microorganism in the slime
(b) Aggregation of slime by microorganisms
(c) Assimilation of phosphorus by microorganisms.

APPENDIX C

IMPROVEMENT IN FILTRATION RATES EFFECTED BY FLOCCULANTS

APPENDIX C

IMPROVEMENT IN FILTRATION RATES EFFECTED BY FLOCCULANTS*

Represents 12 of the best products out of a total of 150 commercial samples tested.

The Filtration Improvement Factor (F.I.F.) is the ratio of the filtration rate for a given flocculated slime to that of untreated slime.

Flocculant	F.I.F.	Optimum Flocculant Conc. in ppm
Amer. Cyanamid Co.		
Reagent S-3000	16	200
Polyacrylamide PAM-50	20	400
Polyacrylamide PAM-75	12	250
Polyacrylamide PAM-100	50	250
Dow Chemical Co.		
Separan 2610	70	200
General Aniline & Film Co.		
PVM/MA (Copolymer of methyl vinyl ether and maleic anhydride) series PVM/MA	30	80
A. F. Goodman & Sons		
Potato starch	9.3	400
Monsanto Chemical Co.		
Lytron 886 (partial Ca salt of copolymer of vinyl acetate and maleic anhydride)	9.0	30
Lytron 886 with 0.05% added $CaCl_2$	50	80
Lytron 887 (copolymer of vinyl acetate and maleic anhydride)	9	30
Morning Star Nicol		
Starch ether: Solvitose H_4	8	800
613-45 (Cationic starch derivative)	8	1500

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Dr. J. W. Bartlett of Battelle-Northwest and Dr. W. M. Goldberger of Battelle-Columbus helped review and edit the report.

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Inorganic Fertilizer and Phosphate Mining Industries - Water Pollution and Control

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27 *Abstract*

A state-of-the-art survey was made of the water pollution problems which result from the production of inorganic fertilizers and phosphate rock. Information required to complete the study was obtained through an extensive literature search, questionnaires sent to the major fertilizer producers, and visits to selected production plants. Ninety eight plants representing thirty three different companies were surveyed. Production figures since 1940 and estimates of production through 1980 were accumulated for phosphate rock and the major fertilizer products. The specific production operations which are the principal generators of contaminated waste waters were identified, and the waste water volumes and compositions for each operation were determined wherever possible. The capability of current technology to treat and control the contaminated waste waters generated by the fertilizer industry was evaluated. Problem areas where additional research and development effort is needed to provide adequate control of waste water discharge were identified. (Fullam - Battelle-Northwest)

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